PB85-115160

Validation of an Emission Measurement Method for Inorganic Arsenic from Stationary Sources: Proposed Method 108 Laboratory and Field Test Evaluations

Research Triangle Inst.
Research Triangle Park, NC

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Oct 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB85-115160

EPA-600/4-84-080
October 1984

VALIDATION OF AN EMISSION MEASUREMENT METHOD FOR INORGANIC ARSENIC FROM STATIONARY SOURCES: PROPOSED METHOD 108

Laboratory and Field Test Evaluations

by

T. E. Ward
Quality Assurance Division
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

R. K. M. Jayanty, P. M. Grohse, W. F. Gutknecht
Research Triangle Institute
Research Triangle Park, North Carolina 27709

C. L. Bruffey, T. J. Wagner, J. W. Prohaska
PEDCo Environmental, Inc.
Cincinnati, Ohio 45246

EPA Contract No. 68-02-3767, Tasks 32, 65, and 66

Project Officer
Thomas E. Ward
Quality Assurance Division
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/4-84-080		PB85 115160

4. TITLE AND SUBTITLE	5. REPORT DATE
VALIDATION OF AN EMISSION MEASUREMENT METHOD FOR INORGANIC ARSENIC FROM STATIONARY SOURCES: PROPOSED METHOD 108 --Laboratory and Field Test Evaluations	October 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) T.E. Ward, R.K.M. Jayanty, P.M. Grohse, W.F. Gutknecht, C.L. Bruffey, T.J. Wagner, J.W. Prohaska	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Research Triangle Institute Research Triangle Park, NC 27709 PEDCo Environmental, Inc. Cincinnati, OH 45246	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO. 68-02-3767 Tasks No. 32, 65 and 66
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency Office of Research and Development Environmental Monitoring Systems Laboratory Research Triangle Park, North Carolina	13. TYPE OF REPORT AND PERIOD COVERED Final
	14. SPONSORING AGENCY CODE EPA/600/08

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The United States Environmental Protection Agency (USEPA) has listed inorganic arsenic emissions as a hazardous air pollutant. USEPA proposed Method 108 for the measurement of these emissions from stationary sources has been subjected to validation studies in this work. Laboratory and field studies were performed. Laboratory studies included analysis of laboratory samples, preparation and analysis of liquid and filter audit samples, and sample stability determinations. Replicate analysis of standards in the laboratory studies indicated a precision of 1.0% in the proposed method. Field studies included determination of the precision of the method in the measurement of inorganic arsenic emissions from stationary sources at the two industries currently subject to the USEPA proposed inorganic arsenic emissions regulations. Based upon the field tests, the precision was 3.85% at a glass plant and 15.7% at a copper smelter. Considering the sampling sites and the variability of process operations, these results indicate a highly acceptable degree of precision. Literature reviews to reveal the sources of emissions are reported. Recommendations are made for improving the method.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Inorganic Arsenic Emissions Stationary Sources Source Test Methods USEPA Method 108		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	95
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

The information in this document has been funded wholly or in part by the U.S. Environmental Protection Agency under Contract No. 68-02-3767 to Research Triangle Institute. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air, implementation of agency-wide quality assurance programs for air pollution measurement systems, and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

Inorganic arsenic emissions are listed by the Agency as hazardous air pollutants, and the Agency has proposed regulation of these emissions. Acceptable measurement methodology is critical for proper assessment of the impact on the environment of these emissions from stationary sources. Development and validation of measurement methods are key components for producing an acceptable method. This study was undertaken to continue development and to validate Method 108, Proposed, for the quantification of inorganic arsenic emissions from stationary sources.

Thomas R. Hauser, Ph.D.
Director
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

ABSTRACT

The United States Environmental Protection Agency (USEPA) has listed inorganic arsenic emissions as a hazardous air pollutant. USEPA Proposed Method 108 for the measurement of these emissions from stationary sources has been subjected to validation studies in this work. Laboratory and field studies were performed. Laboratory studies included analysis of laboratory samples, preparation and analysis of liquid and filter audit samples, and sample stability determinations. Replicate analysis of standards in the laboratory studies indicated a precision of 1.0 percent in the proposed method. Field studies included determination of the precision of the method in the measurement of inorganic arsenic emissions from stationary sources at the two industries currently subject to the USEPA proposed inorganic arsenic emissions regulations. Based upon the field tests, the precision was 3.85 percent at a glass plant and 15.7 percent at a copper smelter. Considering the sampling sites and the variability of process operations, these results indicate a highly acceptable degree of precision. Literature reviews to reveal the sources of emissions are reported. Recommendations are made for improving the method.

CONTENTS

Section		Page
Foreword		iii
Abstract		iv
Figures		vii
Tables		viii
Acknowledgments		ix
1.0	Introduction	1
	1.1 General Information: Arsenic in the Environment	2
2.0	Summary, Conclusions, and Recommendations	4
	2.1 Precision	4
	2.2 Sampling and Analysis	5
3.0	Laboratory Studies	8
	3.1 Literature Review	8
	3.1.1 Arsenic Emissions from Primary Copper Smelters--Background Information for Proposed Standards	8
	3.1.2 Glass Manufacturing Plants--Background Information for Promulgated Standards of Performance, June 1979	11
	3.1.3 Glass Manufacturing Plants--Background Information for Promulgated Standards of Performance, September 1982	12
	3.1.4 Arsenic, Glass Manufacturing--Emission Test Report, Corning Glass Works, Central Falls, Rhode Island	13
	3.1.5 Arsenic, Glass Manufacturing--Emission Test Report, Corning Glass Works, State College, Pennsylvania	14
	3.1.6 A Literature Review on Occurence for Determination of Ni, Cr, Mn and As Species in Air	15
	3.2 Laboratory Evaluation of Method 108	16
	3.2.1 Sample Preparation Procedures	17
	3.2.2 Sample Analysis Procedures	18
	3.2.3 Stability Study	23
	3.2.4 Precision Evaluation of Analytical Portion of Method 108 Measurement	27
	3.2.5 Analytical Observations	27

CONTENTS (continued)

Section		Page
4.0	Field Evaluation	31
	4.1 Plant No. 1	31
	4.1.1 Process Description	31
	4.1.2 Sampling Location and Test Methods	32
	4.1.3 Sampling and Analytical Procedures	37
	4.1.4 Test Results	38
	4.2 Plant No. 2	44
	4.2.1 Process Description	44
	4.2.2 Sampling Location and Test Methods	44
	4.2.3 Sampling and Analytical Procedures	48
	4.2.4 Test Results	48
5.0	Quality Control and Quality Assurance Procedures	61
	5.1 Quality Assurance	61
	5.1.1 Plant Number 1	62
	5.1.2 Plant Number 2	70
6.0	References	79
Appendix A		A-1

FIGURES

Number		Page
4-1	Reverberatory furnace ESP outlet test location	33
4-2	Sediment profile of the ESP outlet duct and location of sample points	35
4-3	Dual-train sampling system showing nozzle, pitot tube, and thermocouple position	36
4-4	Quad-train configuration	45
4-5	Four-train sampling system showing nozzle, pitot tube, and thermocouple position	46
4-6	Furnace exit stack elevation	47

TABLES

Number		Page
3-1	Preparation of Ampules	19
3-2	Quantities of Solid As_2O_3 Loaded Onto Filters	20
3-3	Quantities of Arsenic Loaded Onto Filters in Solution Form	20
3-4	Sample Analysis Result Versus Expected Concentration	22
3-5	Effect of Sample Treatment	24
3-6	Stability Study Data for Filter Samples	25
3-7	Stability Study Data for Impinger Samples	26
3-8	Estimates of the Rate of Change in Concentrations Per Day for Filter Samples	28
3-9	Estimates of the Rate of Change in Concentration Per Day for Impinger Samples	28
3-10	Analytical Results of the Precision Evaluation of Method 108 Measurement	29
4-1	Summary of Arsenic Test Results for Plant No. 1	40
4-2	Statistical Data for Grouped Arsenic Runs at Plant No. 1	42
4-3	Pretest Method 108 Sample Results	50
4-4	Summary of Quad Train Sampling Conditions	51
4-5	Summary of Quad Train Results for Plant No. 2	53
4-6	Statistical Data for Grouped Runs for Plant No. 2	55
5-1	Field Equipment Calibration	63
5-2	Arsenic Blank Data for Plant No. 1 Tests	65
5-3	Audit Results	67
5-4	Arsenic Standard Addition Results	68
5-5	Arsenic Blank Data for Plant No. 2	71
5-6	Arsenic Laboratory Reagent Blank Data for Plant No. 2	73
5-7	Audit Results for Plant No. 2	75
5-8	Duplicate Analyses Data for Plant No. 2	77

ACKNOWLEDGMENTS

Jack C. Suggs contributed to the statistical design of the field test activities and analysis of the data. M. Rodney Midgett and Thomas J. Logan gave advice and comments throughout the project. Alfred E. Vervaert and Ronald E. Myers contributed information on sources and emissions. Gary D. McAlister contributed advice and information on the specific procedures of sampling and analysis. All the above contributions are gratefully acknowledged.

1.0 INTRODUCTION

The United States Environmental Protection Agency (USEPA) has listed inorganic arsenic emissions as a hazardous air pollutant (HAP). National emission standards for hazardous air pollutants are established in accordance with Section 112(b)(1)(B) of the Clean Air Act (42 U.S.C. 7412), as amended. Emission standards under Section 112 apply to new and existing sources of a substance that has been listed as a hazardous air pollutant. A measurement method is needed to determine inorganic arsenic emissions from stationary sources.

The Environmental Monitoring Systems Laboratory (EMSL) has determined the industries and processes of stationary sources which emit significant inorganic arsenic emissions. Included among these are the five most significant sources which were chosen by EPA's Office of Air Quality Planning and Standards (OAQPS) for original consideration for regulation of inorganic arsenic emissions: glass plants; secondary lead smelters; primary copper smelters; cotton ginning activities; and zinc and zinc oxide manufacturing. Presently OAQPS is recommending only primary copper smelters and glass plants for these regulations.

The primary concern of EMSL was validation of the procedure used for sampling and analysis of the arsenic-containing emissions. EMSL determined that the proposed EPA Method 108, which involves collection in impinger solutions and on filters, and measurement using atomic absorption spectrophotometry was the best available method for measuring these arsenic emissions. Therefore, a program to validate this method was designed by EMSL. The validation approach included a multicomponent project which involved both laboratory and field studies. The laboratory studies, which were performed principally at RTI, consisted of the following:

- A review of specific reports provided by EPA to determine typical arsenic emission levels and experience with EPA Method 108, and a review of other potential methods.

- Performance of Method 108 using laboratory samples and evaluation of method components.
- Preparation of audit samples (spiked impinger solutions and filters) for use by EPA.
- Determination of the stability of audit samples.
- Determination of typical emission levels for copper smelters and glass plants and conclusions and recommendations regarding the utilization of EPA Method 108.

Field studies were performed by PEDCo Environmentalists, Inc. These consisted of sampling and analysis of emissions from a copper smelter and a glass manufacturing plant. The principal objectives of these activities were as follows:

- Collection and analysis of emissions including determination of the portions of particulate and vapor phases of arsenic in the stack emissions as determined by Method 108.
- Determination of precision of Method 108 with field samples.
- Identification of potential problems with Method 108 and recommendation of solutions for these problems.

1.1 GENERAL INFORMATION: ARSENIC IN THE ENVIRONMENT

Arsenic is twentieth in abundance in the earth's crust and exists in minerals as the native element including arsenides, sulfides, sulfosalts, arsenites, arsenates, and silicates.[1] Typical minerals are:

realgar, As_2S_2
orpiment, As_2S_3
lollingite, $FeAs_2$
nickel giance, NiAsS
pharmacolite, $CaHAsO_4 \cdot 2H_2O$
mimetite, $3Pb_3(AsO_4)_2 \cdot PbCl_2$.

Arsenic, which is ubiquitous, enters the biosphere through industrial activity or through the use of arsenical products such as pesticides, medicines and feed additives. The three major sources of arsenic in air are smelting of metals from sulfidic ores, burning of coal, vegetation or agricultural wastes, and the use of arsenical pesticides. The arsenic in

air primarily exists as the oxide or one of the salts of the acids. However, it is removed from the air by settling or rainfall and therefore, atmospheric concentrations do not build up. Nonurban areas typically have maximal averages of 20 ng/m^3. However, in regions of high extractive metallurgical activity the concentration can reach 2.5 µg/m^3. Dusts and gases emitted from cotton gins can reach 100 µg/m^3. Burning of the cotton trash also discharges arsenic to the atmosphere.[2]

Approximately 3 percent of the arsenic produced is used as metal in metallurgical alloys of lead and copper. The remaining 97 percent enters end-product manufacture in the form of As_2O_3. Manufacture of end-products for agriculture accounts for about 80 percent of the total consumption of arsenic. As_2O_3 is used to manufacture arsenical pesticides including the arsenate and arsenite salts of lead, calcium, sodium, and the organic arsenicals. The compounds are used in insecticides, herbicides, fungicides, and as desiccants, algecides, sheepdips, wood preservatives, dyestuffs, and veterinary medications. High purity elemental arsenic and arsine (AsH_3) are used by the semiconductor and microelectronic industries.[2]

Arsenic is present as a contaminant in by-product NaCl and Na_2SO_4 from the manufacture of cacodylic acid (dimethyl arsenic acid, $(CH_3)_2$ AsO(OH)) which is used in agriculture. The contaminated salts are recycled and reused or are disposed in a Class 1 landfill.

Arsenic cycling in the environment is constantly changing. It appears everywhere and is constantly being oxidized, reduced or otherwise metabolized. In the soils, insoluble or slightly soluble compounds of arsenic are being resolubilized. Man's activities have modified the arsenic cycle only by causing localized high concentrations.

2.0 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

A multicomponent study was performed which included both laboratory and field studies. Research Triangle Institute reviewed reports describing sampling and analysis of arsenic, evaluated EPA Proposed Method 108 through analysis of laboratory samples, prepared audit samples for field use and studied the stability of audit samples. PEDCo Environmentalists, Inc. collected samples at a copper smelter and a glass manufacturing plant, and analyzed the collected samples.

Several conclusions and recommendations have been made regarding Proposed Method 108 as follows:

- The method is relatively straightforward and is reasonable with respect to time, cost, and precision based upon laboratory and field studies.
- Greater care of the samples during sample preparation and analysis than the proposed method requires should be exercised.
- Graphite furnace atomic absorption techniques have an improved analytical range over hydride techniques, are more rapid, and therefore are recommended to be an adequate measurement substitute.

2.1 PRECISION

The precision of Method 108 is indicated by both laboratory and field work. In the laboratory, replicate analyses of standards showed the precision expressed as the relative standard deviation (RSD) of the analytical method to be approximately 1.0 percent in the 40 to 100 micrograms arsenic per milliter range.

Two field tests to validate proposed Method 108 at different sites were conducted. The first field test was conducted at a primary copper smelter (Plant No. 1) and the second test was conducted at a glass manufacturing facility (Plant No. 2). During the field test series, PEDCo conducted a total of 14 tests of proposed Method 108 (seven paired runs) at Plant No. 1 and a total of 36 tests of proposed Method 108 (nine quad-train runs)

at Plant No. 2 to determine the precision of the methodology for measuring arsenic concentrations. A comparison of the statistical results for total arsenic from Plant No. 1 indicates that the within-run RSD for the seven sample runs ranged between 3.9 and 22.8 percent with the precision expressed as the RSD (coefficient of variation) of the data at 15.7 percent. Standard deviations of paired runs had a low value of 0.36 mg/dNm^3, a high of 4.06 mg/dNm^3, and a pooled mean of 1.90 mg/dNm^3. The mean arsenic concentration of paired runs ranged from 3.08 to 18.3 mg/dNm^3 based on total arsenic, and the overall mean value was 10.5 mg/dNm^3. Considering the sampling site constraints and variable process operation, the results indicate that an acceptable degree of precision was achieved at this source.

The standard deviations of the quad run (Plant No. 2) had a low value of 0.10 mg/dNm^3, a high value of 0.51 mg/dNm^3, and a pooled mean value of 0.37 mg/dNm^3. The RSD values ranged from 0.95 to 5.5 percent with the precision expressed as the RSD (coefficient of variation) of the data at only 3.85 percent. The mean arsenic concentration of the individual quad runs ranged from 9.18 to 10.55 mg/dNm^3 with an overall mean of 9.67 mg/dNm^3, which indicated a generally consistent process operation throughout the test period. Once again, the results indicate that an acceptable degree of precision was achieved. The detailed results of both tests are presented in Section 4.0.

2.2 SAMPLING AND ANALYSIS

Several conclusions and recommendations regarding sample collection and analysis have been proposed. Method 108 sampling specifications for sample collection generally follow those described in EPA Method 5. However, Method 108 analytical procedures for the samples, which require placing the arsenic in the sample into solution and analyzing the solution for arsenic by Atomic Absorption, are vastly different from Method 5.

Thus, sample collection is relatively straightforward for test teams competent in Method 5 sampling. One recommended method revision is to delete the requirement for collection and analysis of sulfur dioxide (SO_2) in the gas streams where the SO_2 concentration is less than 1 percent by volume. This will not have any effect on arsenic determination. OAQPS has eliminated the SO_2 impingers from the proposed Method 108. Alternatively,

the method could include an option to collect the SO_2 in the impinger absorbing solution as a safety measure against short periods of high SO_2 emissions, yet not require sample volume adjustments for an average SO_2 concentration of less than 1 percent. Such an option would result in a maximum error of 1 percent in the arsenic concentration.

The analytical procedures specified in EPA Method 108 were followed during the testing program, except for the following modification. Proposed Method 108 calls for low-level arsenic analysis with an arsine vapor generator. The samples from Plant 1 were analyzed, where applicable, with both the vapor generator and the graphite furnace procedure. The graphite furnace procedure was easier and more accurate. The Plant 2 samples, where applicable, were analyzed with the graphite furnace. Since low-level arsenic analysis by the graphite furnace technique described in EPA Method 206.2[3] gave comparable results, the graphite furnace method was used because of its greater ease and accuracy.

Our recommendation for greater care during sample preparation is based upon the need to avoid bumping and spattering during the evaporation process (explained further in Section 3.2.5). The greater care during sample analysis includes the need to condition the burner head with multiple aspirations when using HF/HNO_3 extracts during sample analysis. Experience gained during sample analysis suggests one procedural addition and one revision to the analytical portion of Method 108. The following precautionary note should be added to the procedure used in the flame analysis of the Parr bomb sample fractions [hydrofluoric acid, nitric acid (HF/HNO_3) extracts]:

> "During the initial flame analysis of a batch of HF/HNO_3 extracts, perform multiple aspirations on the same sample until a stable reading is obtained. The HF in the extract may cause the initial arsenic values to be biased high as a result of dissolution of arsenic residue on the burner head. The multiple aspirations will condition the system."

This precautionary note evolved from the analysis of samples collected at Plant No. 1.

The suggested revision to the analytical portion of Method 108 involves changing the criteria for deciding whether to perform analysis by flame or by the graphite furnace technique. The current version of the method specifies a subsequent furnace analysis if the initial flame analysis yields a concentration of less than 10 mg/liter (ppm) in the digested sample. The use of the furnace technique for these samples is distinctly advantageous for concentrations in the greater range of between 1 and 30 ppm, especially for the HF/HNO_3 bomb fraction. Analyzing these concentrations requires a dilution of 1-to-10 up to 1-to-200. These dilutions eliminate most of the matrix effects in the samples.

Additional quality control procedures that should be added to the method are:

- Prepare and analyze a second solution of 10 percent of the aliquot sample fractions (i.e., rinse and impinger fractions).
- Aspirate or inject a second solution of 10 percent of the filter and bomb fractions.
- Analyze the control sample after every tenth sample. The control sample should be prepared independently of the calibration standards.
- Analyze audit samples in the 5- to 50-ppm range.
- Set up and analyze a blank train.

The standard addition requirement should be retained.

Finally, filter and liquid (impinger) audit samples were studied with regard to stability. Stability as a function of sample type, concentration level and time was evaluated. Changes in concentration were not found to be statistically significant over a six month period for filter type samples except at the highest loading (25 mg). For impinger samples there were no significant losses over the same time period.

3.0 LABORATORY STUDIES

Laboratory studies performed at RTI included a literature review, an evaluation of Method 108, and preparation and stability studies of arsenic audit samples.

3.1 LITERATURE REVIEW

Five documents received from QAD/EMSL were reviewed by RTI with regard to forms and levels of arsenic emitted and the use of Method 108.

3.1.1 Arsenic Emissions from Primary Copper Smelters--Background Information for Proposed Standards, Preliminary Draft, February 1981

This document describes in detail the raw materials and processes used in copper smelting; arsenic distribution and emissions from copper smelters; existing and alternative control technologies; modification and reconstruction and their applicability to primary copper smelters; model plants and regulatory alternatives, environmental impact; costs; and economic impact.

Copper ores are classified as sulfide, oxide, or native, depending upon their predominant minerals. They also contain other metals such as sulfides and oxides of arsenic, iron, antimony, lead, zinc, bismuth, etc. When copper ores are subjected to the preliminary concentration process, other metals such as arsenic are concentrated as well. Arsenic content of copper concentrates processed at U.S. copper smelters varies from a few parts per billion to several percent.

The pyrometallurgical process involves three basic steps:

- Roasting to remove a portion of the concentrate sulfur content,
- Smelting in a furnace to form slag and copper bearing matte,
- Oxidizing of the matte in a converter to form blister copper (~99% Cu).

The form and distribution of arsenic emissions is highly dependent upon process conditions. Arsenic elimination during the smelting process

occurs mainly through volatilization and slagging. Most of the arsenic is volatilized and removed with the offgases. In the presence of oxygen, elemental arsenic and arsenic sulfides are oxidized to the volatile arsenic trioxide, As_2O_3 which sublimes at 193° C. However, under the high-temperature oxidizing roast conditions necessary for sulfur removal, As_2O_3 may be further oxidized to the less volatile As_2O_5 (decomposes at 315° C) which forms stable nonvolatile arsenates that remain in the calcine. Arsenic sulfides present in the copper ore which are oxidized in the roasting process include $FeSAs_2S_3$, As_2S_3, and As_2S_5. Maximum removal of arsenic occurs at lower temperature (500° to 600° C) under reducing conditions. Arsenic is more stable in copper than in Cu_2S, and therefore the volatility of the arsenic in the smelting furnace changes with the grade of matte being produced. When a high grade matte is converted, metallic copper is formed early in the process and acts as a collector for arsenic. As much as 70 percent of the arsenic may appear in the blister copper with only 30 percent eliminated by volatilization or slagging. When a low grade matte is converted, up to 92 percent of the arsenic may be volatilized. Normally, ~70 percent of the arsenic is volatilized in the converter and ~16 percent remains in the slag.

The EPA has performed emissions tests to evaluate available alternative control techniques for control of process and fugitive emissions from process facilities including roasters, smelting furnaces, and converters at primary copper smelters. Eight domestic smelters were tested for arsenic emissions with particulate emissions measurements being conducted at some of the smelters. Arsenic measurements were performed using EPA Method 108. Particulate measurements were performed using EPA Method 5. Each smelter, process, and control device is described and complete analysis results are summarized in the document.

A literature search had revealed that most arsenic emissions from copper smelters were in the form of arsenic trioxide or arsenic pentoxide and that the most commonly used arsenic sampling method was filtration. However, filtration alone was judged to be inadequate for these purposes because of the appreciable vapor pressure of arsenic trioxide. It was decided to determine arsenic collected as a particulate using a Method 5

train with back up impingers containing 0.1 N NaOH. Because of the high concentrations of SO_2 in most gas streams sampled, a series of hydrogen peroxide impingers was placed between the filter and the first basic impinger.

The most commonly used analytical method found in the literature is a wet chemical method based on arsine generation, but copper interferes. Instrumental techniques include atomic absorption (AA), neutron activation, and X-ray fluorescence, but AA was chosen for availability, familiarity and cost considerations. For high concentrations of arsenic, conventional flame AA methods are used. For lower concentrations, a more sensitive technique such as the hydride generator or carbon rod (flameless) system is needed. These conventional and special AA methods were evaluated in terms of precision, accuracy, and sensitivity before testing began and, for the first field test, conventional AA or carbon rod was used, depending upon arsenic concentrations.

After the second field test, the method was reevaluated with the following results:

- No difference was found between the collection efficiencies of 0.1 N NaOH and pure water. Therefore the conventional Method 5 train with water impingers was suggested as an alternate.

- The carbon rod AA Method was found to have precision and accuracy problems when large quantities of dissolved solids are present. The hydride generator technique was found to give more precise and accurate results and was recommended for future use.

- Recovery studies were performed on standard samples and it was found that there is no significant loss of arsenic during the evaporation step of sample preparation.

- The rate of dissolution of arsenic trioxide was found to be slow in all except alkaline solutions. Cleanup procedures for future tests were modified to require that the train be rinsed with 0.1 N NaOH.

- A method of dissolving the entire sample was compared to the less rigorous acid extraction procedure. It was recommended that for future tests filters be analyzed by both methods until conclusive data are obtained.

After additional field testing the final recommendations were: (1) to use the alternate train with H_2O impingers since it was easier to operate and analyze and showed no significant difference in collection efficiency, and (2) to extract filters first using the simple acid extraction method and to extract any undissolved sample with the total dissolution method.

3.1.2 Glass Manufacturing Plants--Background Information for Promulgated Standards of Performance, EPA-450/3-79-005a, June 1979

The glass manufacturing industry has been classified in accordance with the Standard Industrial Classification (SIC) system into four groups:

SIC 3211--Flat glass

SIC 3221--Container glass

SIC 3229--Pressed and blown glass, not elswhere classified (N.E.C.)

SIC 3296--Wool fiberglass

The basic process of high temperature conversion of raw materials into a homogeneous melt can be broken down into three subprocesses: raw material handling and mixing; melting; and forming and finishing. The emissions from furnace operations are greater by two orders of magnitude than those from either the raw materials handling and mixing or the forming and finishing operations. The major type of air pollutant from glass melting is particulate which vaporizes from the molten glass surface and condenses at lower temperatures. Over 75 percent of the particulate catch has a characteristic size of $<1\ \mu$.

Arsenic compounds are included in some batch recipes to aid in "fining" (removing bubbles from the melt) and decolorizing. Arsenic content of raw materials has been reduced in flat glass and eliminated in container glass, but arsenic is still used in the pressed and blown glass industries. Data from OAQPS since June 1979 state that arsenic has been eliminated from flat glass. Arsenic has been assayed in small levels in the particulate emitted from these furnaces in the form of As_2O_3 or As_2O_5. Few test data are available on arsenic emissions. For one test, 80 percent of the arsenic captured was in particulate form. Electrostatic precipitators have been shown to be 99.4 percent effective for total particulate matter, and 42 percent effective in the capture of particulate arsenic.

Emission control techniques discussed in the document include process modifications; all-electric melters; conventional fabric filter systems; venturi scrubbers; electrostatic precipitators; fabric filters with additive injection; and mist eliminators.

3.1.3 Glass Manufacturing Plants--Background Information for Promulgated Standards of Performance, EPA-450/3-79-005b, September 1982

This document presents promulgated standards based on tests conducted in accordance with EPA Method 5 and the Los Angeles Air Pollution Control District Method. The standards reflect the best system of continuous emission reduction and represent levels typically achievable by manufacturers of all types of glass.

The proposed standards were submitted to glass manufacturers for review and comment. Standards for container glass and pressed and blown (soda-lime) glass remained as proposed. The pressed and blown glass industry was divided into three subcategories: borosilicate; soda-lime and lead; and other than borosilicate, soda-lime and lead. The standards for two of these subcategories and for the wool fiberglass and flatglass categories were changed. The reason for the new subcategories is that control device considerations are influenced by process factors with each glass category and subcategory representing a set of process factors.

Most commenters strongly recommended process modification as a means of emission control. These modifications would include lower furnace temperature, electric melting, glass formulation changes and furnace design modifications. However, EPA maintains that there is still uncertainty with regard to the ability of process modifications to control particulate emissions and that the decision to base the New Source Performance Standards (NSPS) on add-on control devices of demonstrated effectiveness is justified. Further information received from OAQPS after September 1982 indicates that EPA in certain instances will consider process modification in lieu of add-on control devices for all categories except lead glass. On the basis of available test reports, EPA concluded that process modifications are still in the research and development stages.

3.1.4 Arsenic, Glass Manufacturing--Emission Test Report, Corning Glass Works, Central Falls, Rhode Island, EMB Report, 78-GLS-3, February 1979

This document describes the testing of the Corning Glass Works plant in Central Falls, Rhode Island. Gaseous and particulate arsenic emissions were determined at a baghouse inlet and outlet to determine the efficiency of the baghouse. Samples of batch and product material, baghouse dust, and slag material were also analyzed for arsenic, and an arsenic material balance was performed. The purpose of the test was to collect data that could be used to support the setting of performance standards for the glass industry. The sampling method used was EPA Method 108, "Reference Method for the Determination of Particulate and Gaseous Arsenic Emissions from Non-Ferrous Smelters." Since only small amounts of SO_2 were present, H_2O_2 was eliminated from the impinger solutions leaving H_2O to trap gaseous arsenic and moisture in the gas stream. Samples were analyzed using atomic absorption spectrophotometry (AAS). Flame AAS was used for samples showing high arsenic levels, while the hydride generation technique was used for low level samples.

The source of the greatest level of pollution from this glass plant is the melt tank, which reaches a temperature of ~1,400° C and is used for conditioning the glass before molding. Melt tank emissions are directed through the plant's emission control equipment and eventually out the stack. Feed batch and feed cullet are mixed with hot cullet return and a solution of arsenic acid in the melt tank. The gas stream leaving the melting tank enters the regenerator where slag is removed. Regenerator exhaust enters the baghouse for particulate removal, and gas from the baghouse is vented to the atmosphere. Arsenic emissions from the stack averaged ~1.65 mg/DNCM (dry normal cubic meter) or 0.05 lb/h. The baghouse capture material averaged 64.0 mg As/g material.

Arsenic material balances for the four runs are summarized below. Batch feed, feed cullet, and return cullet were used to calculate the arsenic "in." Return cullet, molded ware, stack particulate, baghouse-collected particulate, and estimated regenerator condensed particulate were used to calculate the arsenic "out."

Arsenic Material Balance
lb As/h

	Run 1	Run 2	Run 3	Run 4
In	17.11	17.52	16.79	17.20
Out	16.30	16.98	16.79	16.79

3.1.5 Arsenic, Glass Manufacturing--Emission Test Report, Corning Glass Works, State College, Pennsylvania, EMB Report 78-GLS-4, February 1979

This document describes the testing of the Corning Glass Works plant in State College, Pennsylvania. Since there was no port at the inlet to the electrostatic precipitator (ESP), gaseous and particulate arsenic emissions for controlled and uncontrolled conditions were determined by sampling with the ESP electrical current turned on and off, respectively. Samples of batch and product material, ESP dust, and slag material were also collected so an arsenic material balance could be performed. The purpose of the test was to collect data that could be used to support the setting of performance standards for the glass industry. The sampling method used was proposed EPA Method 108, "Reference Method for the Determination of Particulate and Gaseous Arsenic Emissions from Non-Ferrous Smelters." Since only small amounts of SO_2 were present, H_2O_2 was eliminated from impinger solutions leaving H_2O to trap gaseous arsenic and moisture in the gas stream. Samples were analyzed using atomic absorption spectrometry (AAS). Flame AAS was used for samples showing high arsenic levels, while the hydride generation technique was used for low level samples.

Most of the pollution from the plant comes from the melt tank emissions which are passed through the control equipment and eventually go out the stack. The raw material for the glass is approximately 50 percent sand and smaller concentrations of arsenic, lead, silicon, fluorine, aluminum oxide, sodium nitrate, boric acid, and anhydrous borax. Gases from the melting tank are directed through a spray tower and on to the ESP. From the ESP the gases go to the outlet stack.

Arsenic emissions from the stack averaged 0.006 lb/h under controlled conditions. The ESP dust averaged 58.9 mg As/g material.

Arsenic material balances are summarized below. Feed batch and ESP particulate are used to calculate arsenic "in"; ESP particulate, slag, product, and stack emissions are used to calculate arsenic "out."

Arsenic Material Balance
lb As/h

	ESP on			ESP off		
	Run 1	Run 3	Run 5	Run 2	Run 4	Run 6
In	20.34	19.95	19.11	18.66	18.19	19.08
Out	19.84	19.10	19.13	13.56	19.89	20.98

3.1.6 A Literature Review on Occurrence and Methodology for Determination of Nickel, Chromium, Manganese, and Arsenic Species in Air, PB84-172105 (EPA-600/4-84-026), March, 1984

This important document was published in March, 1984 and is reviewed here as it provides information potentially useful to this and future analytical efforts. It reviews the fundamental chemistry of arsenic, its usage and occurances and possible procedures for speciation, that is, determination of individual chemical forms such as arsenite and arsenate.

The chemistry of arsenic is described as follows:

> "Arsenic rarely occurs in the natural environment as the free element, but rather it is associated with sulfide ores in which it occurs as the metal arsenide. Arsenates[3], AsO_4, of aluminum, boron, calcium, cobalt, copper, iron, lead, magnesium, manganese, uranium, and zinc occur naturally, probably as a result of weathering of the arsenide ores. Arsenic is found in rocks (igneous and sedimentary), in soils, in water and in living organisms.
>
> Elemental arsenic can be obtained by the heating of the trioxide with carbon. The most stable form is called grey arsenic or the gamma allotrope. Other allotropic forms which are metastable have been described.[29] The element combines with many metals to form arsenides. It reacts with moist air at ambient temperatures to form a film containing the trioxide. It begins to oxidize in dry air at 200° C. Elemental arsenic reacts with the halogens to form the trihalides. With fluorine, the pentafluoride can also form. Arsenic reacts with sulfur to form As_2S_3, AsS, As_2S_5, and their mixtures. With sulfuric acid arsenic reacts to form the trioxide and SO_2. Hot dilute nitric acid slowly oxidizes arsenic to arsenious acid, H_3AsO_3. Concentrated nitric acid oxidizes it to arsenic acid, H_3AsO_4. No compounds in which arsenic has an apparent oxidation state of 0 are known.

As(-III)--Arsenides of metals are typical compounds in which the oxidation state is -3 and illustrate the element's nonmetallic characteristics. In compounds such as Na_3As, arsenic accepts electrons from true metals and achieves a formal charge of -3.

As(+III)--The +3 oxidation state is the most stable and is characterized by the oxide, As_2O_3, the trichloride $AsCl_3$, the arsenite anion $(AsO_3)^{-3}$ and the sulfides. The vapor of the oxide exists as As_4O_6. The oxide is soluble in bases and acids (amphoteric) and exists as an amorphous glass or as the octahedral forms. As(+III) is readily oxidized to As(V) by hot nitric acid, ozone, hydrogen peroxide, chlorine, bromine, iodine, and alkali hypochlorites. It can be reduced by Fehling's solution, stannous chloride and elemental copper in acid solution.

Arsenites in solution can reduce NO to N_2O. Arsenite salts can exist as orthoarsenites $(AsO_3)^{-3}$, pyroarsenites $(As_2O_5)^{-4}$, metaarsenites $(AsO_2)^{-1}$ and the polyarsenites $(As_4O_7)^{-2}$, $(As_4O_9)^{-6}$, $(As_4O_{11})^{-10}$.

As(V)--As_2O_5 is a diliquescent white powder which dissolves slowly in water and decomposes at red heat to As_2O_3 and O_2. Arsenic acid, $H_3AsO_4 \cdot H_2O$, or acidic solutions of arsenate salts are oxidizing agents and liberate iodine from an iodide and chlorine from hot fuming hydrochloric acid. Salts exist as metaarsenates, $(AsO_3)^{-1}$, orthoarsenates $(AsO_4)^{-3}$ and pyroarsenates $(As_2O_7)^{-4}$. The salts are isomorphous with phosphates."

A number of methods for speciation are described. References to methods involving high performance liquid chromatography with atomic absorption spectrophotometric detection, differential pulse polarography, ion exchange chromatography with atomic absorption spectrophotometric detection and gas chromatography with flame photometric detection are included. Unfortunately, the application of most speciation techniques requires a selective extraction in order not to alter the chemical form of the arsenic compound. The suitability of such techniques at low levels has not been established. Until such procedures have been established and validated, the best approach for characterization of an arsenic source is to measure total arsenic.

3.2 LABORATORY EVALUATION OF METHOD 108

Laboratory studies were conducted to evaluate the performance of Method 108. Standards prepared in the laboratory simulating filter and

impinger materials were used in these tests. The following areas were included in the evaluation:

- The degree of difficulty of the method in terms of both time and required expertise
- Recovery and measurement of audit materials
- Stability of audit materials
- Precision of the method from sample preparation to measurement
- Recommendations regarding analytical aspects of the method.

3.2.1 Sample Preparation Procedures

The purpose of this task was to prepare quality assurance samples for arsenic with loadings approximating emissions expected at field test sites. A concentration matrix was prepared with six different impinger and six different filter loadings. Six samples were prepared at each concentration for a total of 36 impingers samples and 36 filter samples. Concentrations ranged from 0.013 mg to 5.0 mg arsenic for the impingers and ranged from 1.4 mg to 52 mg arsenic for the filters. Ampules were used to contain the impinger samples.

3.2.1.1 Preparation of Standards--

A stock arsenic solution of 1 milligram arsenic per milliliter (1 mg As/mL or 1,000 ppm) was used in the preparation of arsenic quality assurance samples. This stock solution was prepared by dissolving 1.3203 g of arsenic trioxide (As_2O_3 in deionized water adjusted to pH 11 with 0.1N NaOH). The As_2O_3 did not dissolve easily and was mixed for 12 h before completely going into solution. The arsenic solution was neutralized with concentrated nitric acid and diluted to 1.0 L with deionized water. Arsenic standards of 100 and 20 µg/mL were prepared by diluting the stock arsenic solution.

3.2.1.2 Preparation of Ampules--

Gold band type ampules with a capacity of 50 mL were used in preparation of impinger quality assurance samples. The ampules were cleaned by successive washings with soap and water, a 1:1 mix of nitric acid, deionized water, tap water, and deionized water. They were then air-dried.

Each set of ampules was prepared according to Table 3-1. Class A glass pipets were used for all additions of standards and deionized water with the exception of quantities less than 1 mL. In those cases, an adjustable pipet (0-1.0 mL) was used. Prepared ampules were covered with Parafilm and refrigerated prior to being sealed.

3.2.1.3 Preparation of Filters--

Reeve Angle glass fiber filters, grade 934AH, cut down to 8 centimeters diameter were used in preparing the arsenic quality assurance samples. The filters were suspended on ring supports which had been covered with Parafilm.

For the lower concentrations (filter sets C and F) arsenic was applied in the form of stock arsenic solution (1 mg As/mL). Care was taken to avoid spreading the solution to the area of the filter in contact with the ring support. To prevent saturation of the filters, the solution was added in quantities of one milliliter or less and the filters were allowed to dry for 10-15 min between applications.

For the higher concentrations (filter sets A, B, D, and E), arsenic was applied in the form of solid As_2O_3. A quantity of As_2O_3 was weighed onto a watchglass on a Mettler microbalance and transferred onto the filter by rinsing the watchglass with 0.5-mL increments of deionized water. Wetting the filter with 0.5 mL of deionized water prior to adding the As_2O_3 helped keep the solid material on the filter. A total of 2 mL of deionized water was applied at 10-min intervals.

All filters were transferred from the ring supports to clean Petri dishes for storage. Tables 3-2 and 3-3 detail the quantities of As_2O_3 loaded onto the filters.

3.2.2 Sample Analysis Procedures

3.2.2.1 Ampule Samples--

Selected ampules from each concentration set were prepared for analysis by atomic absorption spectrophotometry (AA) to check the accuracy of sample preparation. Each ampule was drained into a 500-mL volumetric flask and diluted to exactly 500 mL with deionized water. A 50-mL portion of this solution was then pipeted into a 150-mL beaker. Following addition of 10 mL of concentrated nitric acid, the solution was brought to a boil and evaporated to dryness. After cooling, 5 mL of 50% nitric acid were added

TABLE 3-1. PREPARATION OF AMPULES

Ampule no.	Total arsenic in ampule, mg	Arsenic standard, ppm	Volume of standard, mL	Volume deionized water, mL
A-1-I-A-6-I	1.000	1000	1.0	49.0
B-1-I-B-6-I	5.000	1000	5.0	45.0
C-1-I-C-6-I	0.200	100	2.0	48.0
D-1-I-D-6-I	0.067	100	0.67	50.0
E-1-I-E-6-I	0.333	100	3.33	47.0
F-1-I-F-6-I	0.013	20	0.65	50.0
G-1-I-G-6-I	50.00	1000	50.0	--
H-1-I-H-6-I	20.00	1000	20.0	30.0

TABLE 3-2. QUANTITIES OF SOLID As_2O_3 LOADED ONTO FILTERS

Filter no.	As_2O_3 loaded, mg	Filter no.	As_2O_3 loaded, mg
A-1-F	6.807	D-1-F	10.689
A-2-F	7.059	D-2-F	14.938
A-3-F	7.872	D-3-F	11.394
A-4-F	6.819	D-4-F	8.411
A-5-F	10.257	D-5-F	15.609
A-6-F	10.017	D-6-F	13.417
B-1-F	36.852	E-1-F	51.329
B-2-F	31.389	E-2-F	49.441
B-3-F	37.001	E-3-F	49.354
B-4-F	32.769	E-4-F	50.606
B-5-F	32.781	E-5-F	52.146
B-6-F	32.808	E-6-F	50.274

TABLE 3-3. QUANTITIES OF ARSENIC LOADED ONTO FILTERS IN SOLUTION FORM

Filter no.	As_2O_3 loaded, mg	Filter no.	As_2O_3 loaded, mg
C-1-F	1.400	F-1-F	2.000
C-2-F	1.400	F-2-F	2.000
C-3-F	1.400	F-3-F	2.000
C-4-F	1.400	F-4-F	2.000
C-5-F	1.400	F-5-F	2.000
C-6-F	1.400	F-6-F	2.000

and the solution was warmed with stirring for a few minutes. This solution, after cooling, was diluted to 50 mL with deionized water. Samples were stored in Nalgene bottles until analyzed by AA. Table 3-4 shows the analysis results versus expected concentration. The data indicate that the procedure for preparation of liquid samples in ampules is satisfactory. The data indicate that preparation of filter samples required further study. This additional study was performed during the stability studies described in Section 3.2.3 and it is concluded that the procedure is acceptable.

3.2.2.2 Deionized Water Blank and 0.1N NaOH Blank--

Fifty milliliters of deionized water and 50 mL of 0.1N NaOH were separately prepared as impinger samples but were not initially diluted to 500 mL. These were used as background checks.

3.2.2.3 Filter Samples--

Selected filters from each concentration group were prepared for analysis by atomic absorption spectrophotometry. Each filter was removed from the Petri dish, folded with the solid material on the inside, and transferred to a 150 mL beaker. Any solid material which may have fallen off the filter was added to the beaker. A 50-mL portion of 0.1N NaOH was added and the solution warmed at low heat for fifteen minutes with occasional stirring. To this was added 10 mL of concentrated nitric acid, the solution brought to a boil, and simmered for 15 min. This solution was filtered through a Whatman No. 41 filter into a 150 mL beaker. The filter was washed with 50 mL of hot water. This filtrate was boiled and evaporated to dryness. Care was taken to prevent splattering as the beaker neared dryness. When dry, the beaker was cooled, 5 mL of 50% HNO_3 was added, and the solution warmed and stirred. After cooling, this solution was diluted to 50 mL with deionized water. Samples were stored in Nalgene bottles until analyzed. Table 3-4 shows analysis results versus expected values.

3.2.2.4 Filter Blank--

A Reeve Angle filter was cut in strips and placed in a 150-mL beaker. It was later treated according to the procedure used for sample filters.

TABLE 3-4. SAMPLE ANALYSIS RESULT VERSUS EXPECTED CONCENTRATION

Ampule no.	Concentration expected, ppm[a]	Concentration by AA, ppm	Filter no.	Concentration expected, ppm[b]	Concentration by AA, ppm
A-5-I	2.000	1.82	A-5-F	155.37	166
A-6-I	2.000	2.03	A-6-F	151.73	140
B-5-I	10.000	8.83	B-2-F	475.47	443
B-6-I	10.000	8.93	B-5-F	496.55	487
C-5-I	0.400	0.408	C-5-F	28.00	22.2
C-6-I	0.400	0.360	C-6-F	28.00	24.5
D-5-I	0.134	0.123	D-2-F	266.27	205
D-6-I	0.134	0.122	D-5-F	236.44	215
E-5-I	0.666	0.592	E-5-F	789.89	780
E-6-I	0.666	0.626	E-6-F	761.53	760
F-5-I	0.026	0.027	F-5-F	40.00	40.0
F-6-I	0.026	0.026	F-6-F	40.00	32.7

[a]Total mg As in the ampule diluted to 500 mL = ppm expected.

[b]Total mg As on the filter diluted to 50 mL.

3.2.2.5 Analysis of Standards Versus Treated Standards--

Aliquots of the standards used for sample preparation were treated like impinger samples and compared to untreated standards. Standards of 20 µg/mL, 100 µg/mL and 1000 µg/mL were used. A 50 mL aliquot of each was used and each standard treated according to the procedure for preparing impingers for analysis by AA, except that they were not diluted to 500 mL. Results for prepared standards versus untreated standards are presented in Table 3-5. The results in Table 3-5 indicate no effect upon recovery by the Method 108 sample treatment procedure.

3.2.3 Stability Study

The stability of both simulated sample types (impinger and filter) for potential use as audit materials for EPA proposed Method 108 were evaluated over a six (6) month period. Three levels of arsenic concentration were prepared for each sample type with twelve (12) samples corresponding to each concentration level. Immediately after these samples were prepared, three (3) at each concentration level of both sample types were digested and analyzed to establish a "Day 0" concentration. After one month three additional samples of each concentration and type were digested and analyzed. This procedure was repeated at the three (3) month interval and finally at the end of six (6) months. Sample loadings and analytical results are indicated in Tables 3-6 and 3-7 for filter and impinger sample types respectively. Results of a statistical analysis of the stability data are discussed below.

3.2.3.1 Statistical Analysis--

The basic model used in the statistical analysis of this data is

$$Y_d = \alpha + \beta d + e_d$$

where d = day on which the sample was analyzed, and

Y_d = measured concentration on day d

In this model α and β are parameters which represent the intercept and slope, and e_d is an error term which includes deviations from the assumed model and errors in making the measurements. The model assumes that the

TABLE 3-5. EFFECT OF SAMPLE TREATMENT

Concentration standards, (µg/mL)	Analysis of untreated standards, µg/mL	Analysis of treated standards, µg/mL
20	19.48	21.71
100	103.33	100.00
1000	923.08	961.50

TABLE 3-6. STABILITY STUDY DATA FOR FILTER SAMPLES

Filter no.	Milligram arsenic loaded	Milligrams arsenic recorded			
		Day 0	Day 29	Day 85	Day 170
X-1-F	2.00	2.17			
X-2-F	2.00	1.88			
X-3-F	2.00	2.19			
X-4-F	2.00		1.95		
X-5-F	2.00		1.96		
X-6-F	2.00		1.91		
X-7-F	2.00			1.96	
X-8-F	2.00			1.93	
X-9-F	2.00			1.99	
X-10-F	2.00				1.90
X-11-F	2.00				1.96
X-12-F	2.00				2.00
Y-1-F	9.102	8.97			
Y-2-F	8.037	8.26			
Y-3-F	7.201	7.30			
Y-4-F	7.722		7.00*		
Y-5-F	7.048		6.45*		
Y-6-F	8.068		6.95*		
Y-7-F	7.226			7.15	
Y-8-F	8.128			8.15	
Y-9-F	7.301			7.35	
Y-10-F	7.450				7.30
Y-11-F	7.550				6.90
Y-12-F	7.330				7.25
Z-1-F	27.219	31.3*			
Z-2-F	27.924	32.3*			
Z-3-F	25.485	27.8*			
Z-4-F	26.460		24.4		
Z-5-F	26.366		22.9		
Z-6-F	27.214		24.8		
Z-7-F	26.436			25.7	
Z-8-F	26.239			24.9	
Z-9-F	27.969			25.5	
Z-10-F	26.543				25.2
Z-11-F	26.640				24.8
Z-12-F	26.646				24.8

*Suspect data - a possible analytical problem may have existed.

TABLE 3-7. STABILITY STUDY DATA FOR IMPINGER SAMPLES

Impinger No.	Concentration in µg As/mL loaded	Concentration in µg As/mL recovered			
		Day 0	Day 29	Day 86	Day 170
U-5-I	5.00	5.27			
U-7-I	5.00	5.26			
U-12-I	5.00	5.44			
U-1-I	5.00		5.95*		
U-2-I	5.00		5.77*		
U-3-I	5.00		5.58*		
U-4-I	5.00			5.40	
U-6-I	5.00			5.19	
U-8-I	5.00			5.87	
U-9-I	5.00				4.99
U-10-I	5.00				5.28
U-11-I	5.00				5.20
V-5-I	0.500	0.435			
V-8-I	0.500	0.442			
V-9-I	0.500	0.533			
V-1-F	0.500		0.507		
V-2-I	0.500		0.489		
V-3-I	0.500		0.746*		
V-4-I	0.500			0.541	
V-6-I	0.500			0.365*	
V-7-I	0.500			0.541	
V-10-I	0.500				0.507
V-11-I	0.500				0.507
V-12-I	0.500				0.555
W-2-I	0.0500	0.0290*			
W-11-I	0.0500	0.0298*			
W-12-I	0.0500	0.0307*			
W-1-I	0.0500		0.0560		
W-3-I	0.0500		0.152*		
W-4-I	0.0500		0.094*		
W-5-I	0.0500			0.0514	
W-6-I	0.0500			0.0504	
W-7-I	0.0500			0.0477	
W-8-I	0.0500				0.0499
W-9-I	0.0500				0.0486
W-10-I	0.0500				0.0520

*Suspect data - a possible analytical problem may have existed.

rate of change in concentration per day (represented by parameter β) is constant over the period of observation.

The amount of arsenic loaded in the sample was treated as the measurement for day 0 and the day 0 measurement was treated as the measurement for day 1 for sample sets Y and Z. Two types of analyses were performed; the first included all data for a given sample type and the second excluded "suspect" data. "Suspect" data were those generated when possible analytical problems existed on a given date. These data are indicated in Tables 3-6 and 3-7 by asterisks. Data on each impinger or filter type (whether "suspect" or otherwise) were analyzed separately. The estimates of the rate of change in concentration per day are given in Table 3-8 for filter samples and in Table 3-9 for impinger samples.

As noted, in the stability evaluation process, a linear regression model was fit to the analysis data collected over time. The objective of these calculations was to determine whether or not the calculated slopes, that is, changes in concentration with time, were significantly different from zero. These rates of change per day and their relative slopes for the majority of sample types and concentration levels proved not to be significant at the $p = 0.05$ level. However, filter sample set Z does demonstrate a trend toward decreasing values with the largest change apparently occurring during the first month.

3.2.4 Precision Evaluation of the Analytical Portion of Method 108 Measurement

The precision of the analytical portion of method 108 was determined from triplicate analyses of each of two arsenic stock solutions, 40 and 100 µg As/mL. Three 50-mL aliquots of each stock solution were digested and analyzed by flame atomic absorption (nitrous oxide-acetylene). The analytical results are indicated in Table 3-10. At both concentration levels good precision (RSD) was observed (1.0 percent).

3.2.5 Analytical Observations

The method is relatively straightforward and presents few problems for the analyst. The following are some observations.

TABLE 3-8. ESTIMATES OF THE RATE OF CHANGE IN CONCENTRATION PER DAY FOR FILTER SAMPLES

Filter samples	Rate of change $\times 10^{-3}$ (mg As/day)	p-Value
X	- 0.5	0.28
Y	- 3.3 (- 3.5)*	0.15 (0.10)*
Z	-15.8 (-10.5)*	0.02 (0.01)*

*Excluding suspect data.

TABLE 3-9. ESTIMATES FOR THE RATE OF CHANGE IN CONCENTRATION PER DAY FOR IMPINGER SAMPLES

Impinger samples	Rate of change $\times 10^{-3}$ ($\mu g\ As\ mL^{-1}\ day^{-1}$)	p-Value
U	- 2.0 (- 1.0)*	0.15 (0.44)*
V	+ 0.02 (+ 0.3)*	0.97 (0.18)*
W	- 0.04 (-0.02)*	0.80 (0.25)*

*Excluding suspect data.

TABLE 3-10. ANALYTICAL RESULTS OF THE PRECISION EVALUATION OF METHOD 108 MEASUREMENT

Sample no.	As concentration, µg/mL		Difference Δ, percent	Relative standard* deviation, %
	Expected	Measured		
20 F_A	40.0	39.6	-1.0	
20 F_B	40.0	39.9	-0.3	0.8
20 F_C	40.0	40.2	+0.5	
50 F_A	100.0	99.5	-0.5	
50 F_B	100.0	101.7	+1.7	1.2
50 F_C	100.0	99.9	-0.1	

*Relative Standard Deviation, % = $\dfrac{\left(\dfrac{n\Sigma x^2 - (\Sigma x)^2}{n\,(n-1)}\right)^{\frac{1}{2}}}{\bar{X}}(100)$

Section 4.3.1 of the Method 108 describes the digestion of filter materials. Following the filtration, the filtrate is evaporated to dryness. As stated earlier, the evaporation process must be performed with extreme care to avoid "bumping" or "spattering" of the concentrate resulting in possibly significant losses. Therefore, the heating process should be slowed when less than 10 mL of liquid volume remains. This precaution does not apply as severely to impinger or rinse type samples.

The measurement methods of choice are described in the method as either flame atomic absorption or hydride generation atomic absorption. This approach, however, leaves an analytical gap in terms of range in the high ppb (µg/L) to low ppm (µg/mL) region (of the filter digest or impinger solution) that is possibly inconvenient to the analyst. As a consequence, graphite furnace techniques (GFAA) are recommended as a substitute measurement method for the low ppb to low ppm concentration range. GFAA methods for arsenic can achieve detection limits within an order of µg/L magnitude of the hydride technique. In addition, the method is considerably more rapid and at least as simple as hydride techniques. As a consequence, it is suggested that the technique could be legitimately substituted for hydride techniques altogether.

4.0 FIELD EVALUATION

As noted, the primary objectives of the field testing program were to determine the precision of Method 108 expressed as relative standard deviation (coefficient of variation) based on the results of the dual and quad train sample runs and to develop or refine quality assurance guidelines necessary to obtain reproducible and representative test data. Two field tests at different sites were conducted. The first field test was conducted at a copper smelter (designated plant No. 1) from September 14 through 16, 1983, and the second test was conducted at a glass manufacturing facility (designated Plant No. 2) from May 14 through 16, 1984. This section briefly summarizes the process descriptions, sampling locations, test methods, and the test results obtained from the two sources. A detailed description of the processes, sampling locations, test methods, and the field data sheets from the two sources are presented in two separate reports.[4 5]

4.1 PLANT NO. 1

4.1.1 Process Description

The smelter processes copper ore concentrates, precipitates, and smelter byproducts from numerous domestic and foreign sources. This custom smelter produces about 320 Mg (353 tons) of anode copper per day at full smelt and houses the only arsenic production facility in the United States. The copper smelter facilities include ten roasters, two reverberatory smelting furnaces, three Pierce-Smith converters, and two tilting anode furnaces. Arsenic production facilities consist of three Godfrey roasters, three arsenic trioxide (As_2O_3) settling chambers, storage facilities, and a metallic arsenic plant. According to EPA estimates, the contributions from the No. 2 reverberatory furnace and the metallic arsenic plant constitute 95 percent of the total arsenic emitted to the atmosphere via the main stack.

Tests were performed using existing sampling ports located on top of the rectangular brick breeching connecting the reverberatory furnace ESP outlet with the main stack.

Each of the smelter's two reverberatory smelting furnaces has an approximate capacity of 1,090 Mg (1,200 tons) of calcine per day. Almost exclusively, the furnace evaluated is the one used for production. It is 33.5 m (110 ft) long and 9.8 m (32 ft) wide and is fired by either oil or natural gas. During furnace charging, the larry cars are discharged through one of four Wagstaff guns located along the furnace side walls. Less than 1 minute is normally required to discharge one car. At full smelt, two cars are discharged about every 15 minutes. The maximum furnace charge rate, or full smelt, is defined by the number of charges (loads) per hour to the furnace. A charge rate of six loads per hour, or 34.2 Mg (38 tons) per hour, was established as the baseline condition for determining the furnace production status. Calcine charge rates greater than six loads per hour were considered representative of maximum production rates. During the testing period the calcine charge rate varied. The first test run was conducted at an average calcine charge rate (~6 charges/h), the second run at a low charge rate (~4 charges/h), and the third through seventh runs at a high charge rate (>6 charges/h), as determined from data recorded by EPA personnel.

4.1.2 Sampling Location and Test Methods

During the test series, PEDCo conducted a total of 14 tests (seven paired runs) at this location to determine the precision of the methodology for measuring arsenic concentrations by using procedures described in EPA Methods 1 through 5[6] and proposed Method 108.[7] A dual-train, single-point, isokinetic sampling technique was used.

All tests were conducted by using existing sampling ports located on top of the rectangular brick breeching connecting the ESP outlet with the main stack. Figure 4-1 presents a schematic of the sampling location. Because of the geometric configuration of the ductwork and the location of the flow-control dampers and corresponding structural supports, the sampling location did not meet the minimum requirements specified in EPA Reference

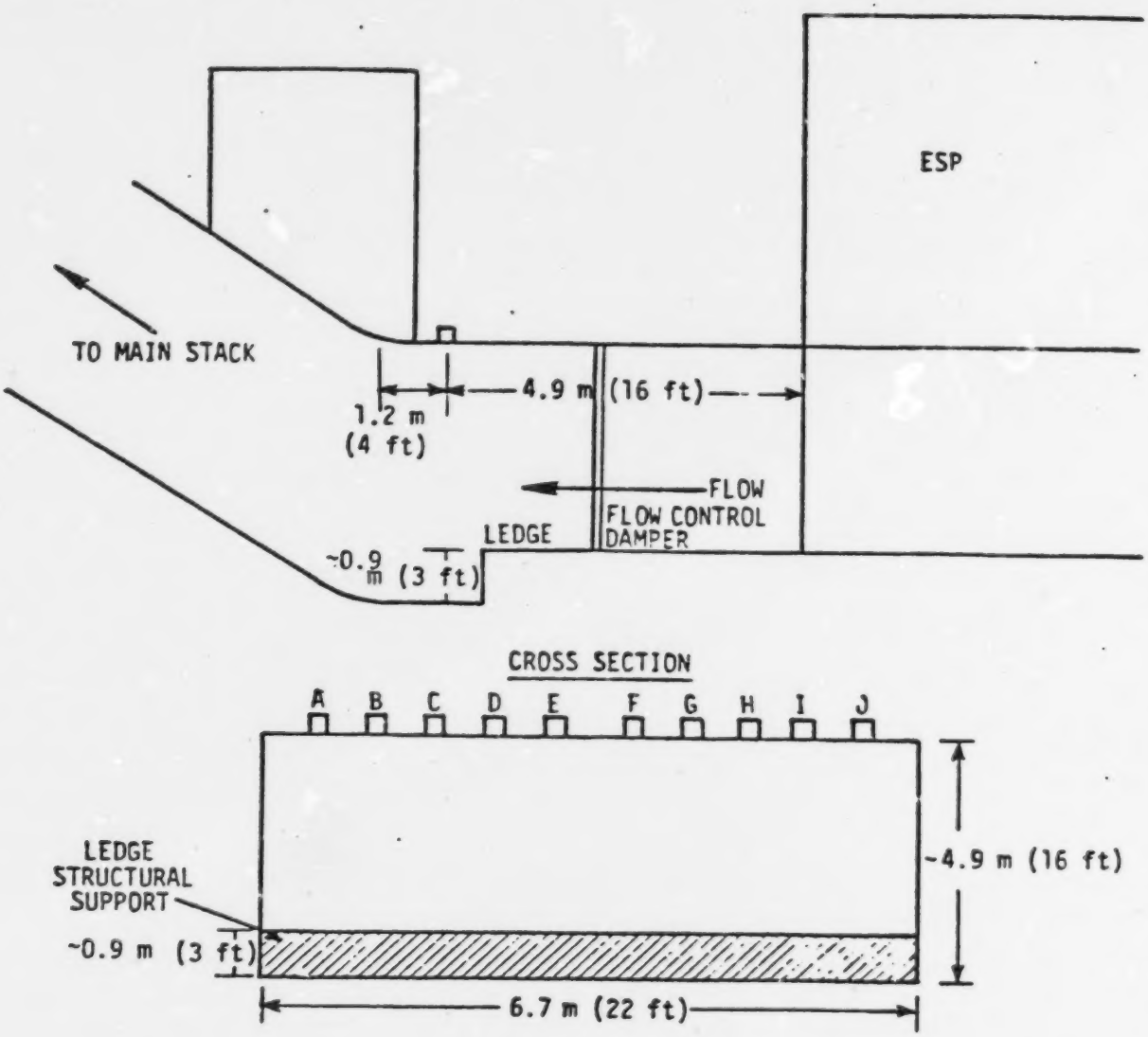


Figure 4-1. Reverberatory furnace ESP outlet test location.

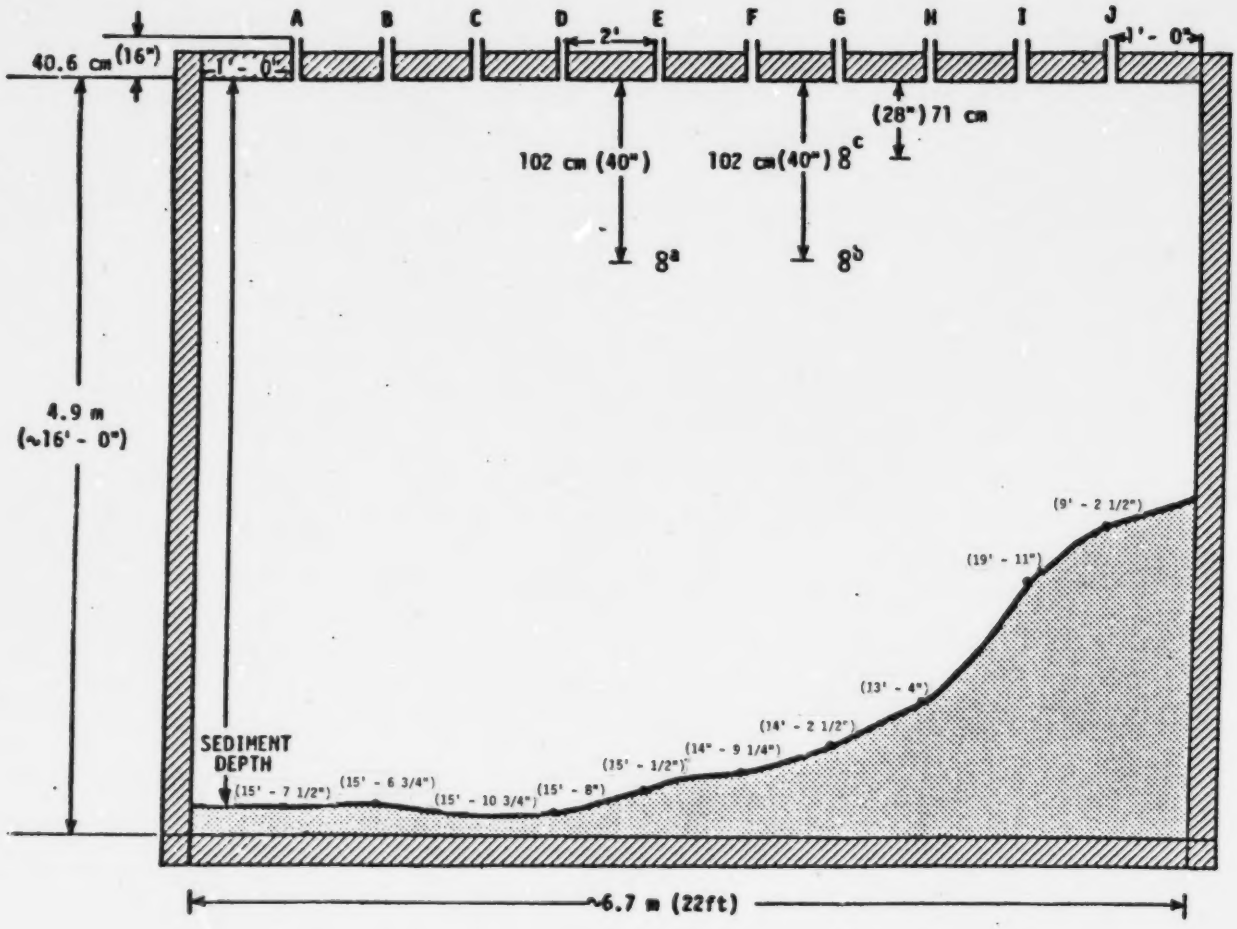
Method 1.[3] Because the dual train sampling nozzles were very close to each other (5 cm) during each of the seven runs, thereby effectively making them coincidental single point sampling devices, this location is acceptable for purposes of establishing precision of the proposed Method 108. This site was the only available location for access to the total cross-sectional area of the ESP outlet breeching.

Ten 6.4 × 9.5 cm (2.5 × 3.75 in.) sampling ports were equally spaced on 61-cm (24-in) center sections across the 6.7-m (22-ft) wide rectangular brick breeching. The depth of each sampling port casing was variable and ranged from 38 to 43 cm (15 to 17 in.).

Figure 4-2 presents a schematic of the flue cross section and location of sampling points for the dual sampling trains. An uneven deposition of materials on the bottom of the flue posed problems in establishing a velocity profile of the cross-sectional area of the duct. Accordingly, the sediment depth at each sampling port was determined by first measuring the distance from the top of the sampling port casing to the top layer of sediment and subtracting the nominal depth of the port casing. These values are recorded in parentheses for each sampling port in Figure 4-2.

A velocity and temperature profile was established according to procedures described in EPA Method 2.[6] Based on the sediment depth information contained in Figure 4-2, a 150-point matrix was established with traverse points located at 0.3-m (1-ft) increments in each sampling port. Of the 150 points, 15 could not be measured because of the sediment.

The gas-velocity head and temperature-profile data were used in the selection of a general sampling area where both nozzles could be positioned at points of equal velocity to minimize spatial variations in emissions. A total of three different sampling points (a, b, c) were used over the course of the test series as depicted in Figure 4-2. Figure 4-3 depicts the dual-train nozzle arrangement used in these tests. During these runs, sample rates ranged from 0.012 dry normal cubic meters (dNm^3)/min (0.42 dscf/min) to 0.039 dNm^3/min (1.38 dscf/min), and typical sampling times were 60 min. Runs AEOD-1 and 2 were conducted for 115 min.



a THIS SAMPLE POINT WAS USED FOR RUN NO. AEOD - 1
b THIS SAMPLE POINT WAS USED FOR RUN NOS. AEOD - 2 THROUGH 6
c THIS SAMPLE POINT WAS USED FOR RUN NO. AEOD -7

Figure 4-2. Sediment profile of the ESP outlet duct (cross section) and location of sample points (no scale).

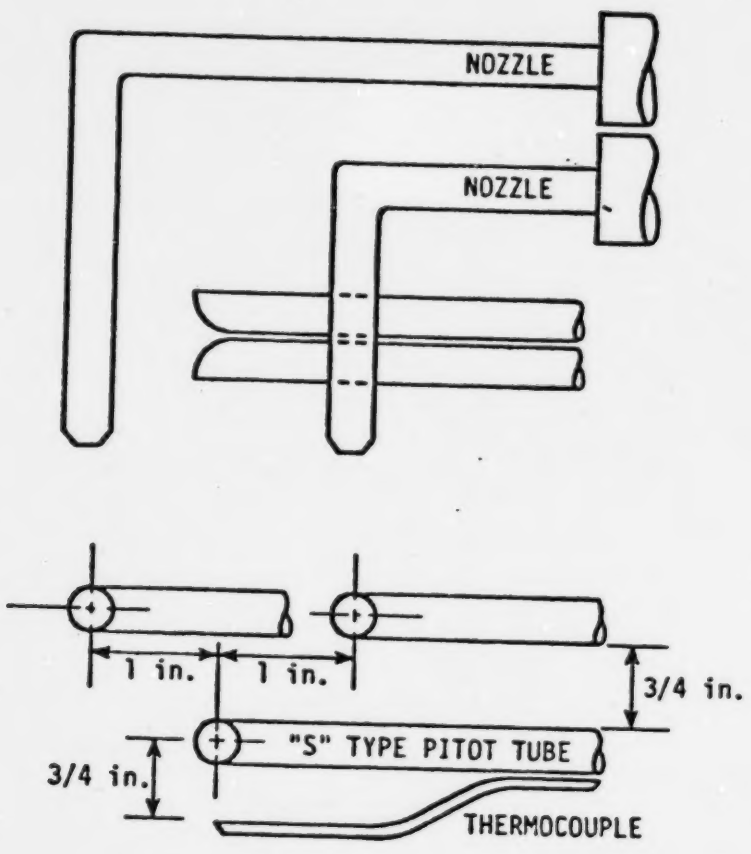


Figure 4-3. Dual-train sampling system showing nozzle, pitot tube, and thermocouple position.

4.1.3 Sampling and Analytical Procedures

The sampling and analytical procedures used in this test program followed those described in EPA Reference Methods 1 through 5[6] and proposed Method 108[4] as detailed in the QA Project Plan prepared by PEDCo and reviewed by EMSL. The procedures, described briefly here, are presented in a separate report.[4,5]

4.1.3.1 Velocity and Gas Temperature--

A Type-S pitot tube and an inclined draft-gauge manometer were used to measure gas velocity pressures at the test sites. Temperature was measured with a thermocouple and digital readout. During each sample run, velocity and temperature measurements were taken at a single sampling point in the duct. Prior to each test series, separate velocity measurements were taken by traversing the entire sample cross-sectional area to determine an average value. Measurements were taken in accordance with procedures outlined in EPA Reference Method 2.[6]

4.1.3.2 Molecular Weight--

Flue gas composition was determined in accordance with the basic procedures described in EPA Reference Method 3.[6] Grab samples were collected before any sampling began to establish baseline contents of oxygen, carbon dioxide, and carbon monoxide. Bag samples were collected at least twice daily during sampling at each source and analyzed with an Orsat gas analyzer. Based on the SO_2 concentration determined by the Method 108 sampling train, carbon dioxide results at Plant No. 1 were corrected for SO_2. This correction was made because SO_2 would be included in the Orsat-generated CO_2 value, which would cause a bias in CO_2 results. The SO_2 content in the gas stream typically measured less than 0.3 percent by volume, and the gas composition at the test site remained consistent throughout the test series.

4.1.3.3 Arsenic--

Method 108[7] was used to measure arsenic concentrations. All tests were conducted isokinetically by regulating the sample flow rate relative to the gas velocity in the duct (as measured by the pitot tube and thermocouple attached to the dual sampling probe). Each individual sampling train consisted of a heated glass-lined probe, a 61-cm (21-in.)-long heated

glass connector, a heated 7.6-cm (3-in.)-diameter glass fiber filter (Whatman Reeve Angel 934AH), and a series of six Greenburg-Smith impingers followed by a vacuum line, vacuum gauge, leak-free vacuum pump, dry gas meter, thermometers, and a calibrated orifice. The two identical sampling trains were so positioned that the nozzles were 5 cm apart in the gas stream. The probe and filter were heated to approximately 121° C (250° F).

The nozzle, probe, and filter holder portions of the sampling train were rinsed with 0.1 N NaOH at the end of each test. The filter and NaOH rinse were prepared, combined, and analyzed for arsenic by atomic absorption.

The amount of water collected in the impinger section of the sampling train was measured gravimetrically at the end of each sample run to determine the moisture content of the flue gas. The contents of the first two impingers, each of which had been charged initially with 150 mL of distilled water, were transferred to a polyethylene container. These impingers and all connecting glassware, including the back half of the filter holder, were rinsed with 0.1 N NaOH, and the rinse was added to the container. The contents of the third, fourth, and fifth impingers, which initially had been charged with a total of 600 mL of hydrogen peroxide, were transferred to a polyethylene container. The impingers and all connecting glassware were rinsed with distilled water, and this rinse was added to the container. The contents of the first two impingers and 0.1 N NaOH rinse were analyzed for arsenic by atomic absorption. The contents of the third, fourth, and fifth impingers and distilled water rinse were titrated on site with 1 N NaOH to determine SO_2 concentrations.

4.1.4 Test Results

A total of 14 tests (seven paired-train runs) were conducted using EPA Method 108[4] to measure arsenic concentrations. All tests were conducted by using single-point, isokinetic sampling techniques. Two identical trains were so positioned that the nozzles were approximately 5 cm (2 in.) apart in the gas stream. This type of placement for nozzles has been shown previously[8] and should be considered identical points for sampling purposes. Gas velocity and temperature data were used to select a general sampling area where both nozzles could be positioned at points of equal velocity to minimize spatial and temporal variations in emissions.

Table 4-1 presents sampling and analytical results of the seven paired sample runs. The sample volumes used in all test calculations have been corrected for the concentration of SO_2 in the gas stream that was collected by the sampling trains according to Method 108 procedures even though the measured concentrations of sulfur dioxide (SO_2) varied from less than 0.1 percent up to a maximum of ~0.3 percent by volume.

These levels of SO_2 did not present a safety hazard to test personnel or a serious potential for damage to equipment. These tests could have been conducted effectively without using the hydrogen peroxide (H_2O_2) impingers to collect the SO_2, which would have eliminated the need to adjust metered sample volumes. A small error in molecular weight determination would result from not correcting the carbon dioxide (CO_2) concentration measured by Orsat analysis for the amount of SO_2 retained in the CO_2 Orsat absorbing reagent. The error in molecular weight would carry over to the emission rate and isokinetic calculations; however, for an SO_2 concentration of 1 percent by volume, not adjusting the CO_2 concentration would result in an error in emission rate and isokinetic rate of less than 0.5 percent. When the SO_2 concentration is 1 percent or less, the error in emission rate and isokinetic rate determinations would be less than approximately 1.5 percent if the sampling train was set up to collect SO_2 (i.e., H_2O_2 solution was used in the backup impingers), and the corresponding adjustments for SO_2 were not made to either metered sample volume or CO_2 concentrations measured by Orsat.

Sample volumes ranged from 1.09 to 2.25 dNm^3. Isokinetic sampling rates were all between 98 and 108 percent, which is within the acceptable range of 90 to 110 percent. Probe and filter temperatures were maintained at approximately 121° C. The moisture content of the stack gas at the sampling point was consistent, and the gas temperature ranged between 88° and 106° C.

The arsenic sample weights are shown for each sample fraction; however, the filter weights include both the sodium hydroxide (NaOH) extract and the Parr bomb (HF/HNO_3 extract) results. The Parr bomb results constituted between 5 and 20 percent of the total arsenic in the filter sample.

The distribution of arsenic between the front half of the sampling train (filter and probe rinse) and back half (impingers) varied, as the

TABLE 4-1. SUMMARY OF ARSENIC TEST RESULTS FOR PLANT NO. 1

AEOD Run No.	Date (1983) and time	Sampling volume, dNm^3[a]	Gas temperature at sampling point, °C	Percent moisture	Gas velocity at sampling point, m/s	SO_2 concentration, ppm by volume	Arsenic sample weight, mg					Concentration, mg/dNm^3			Isokinetic rate, percent
							Filter[b]	Probe rinse	Total front half	Back half	Total	Front half	Back half	Total	
1A	9/15	1.371	106	6.4	5.5	2660	3.88	2.63	6.51	4.93	11.44	4.75	3.60	8.34	108
1B	21:27-23:22	1.360		7.0		2194	4.91	3.06	7.97	2.51	10.48	5.86	1.84	7.70	103
2A	9/15	2.332	88	5.7	8.8	851	1.68	2.15	3.83	3.94	7.77	1.64	1.69	3.33	106
2B	01:43-03:38	2.251		5.8		882	1.73	1.05	2.78	3.58	6.36	1.24	1.59	2.82	103
3A	9/16	1.294	106	6.0	10.4	2767	4.74	5.81	10.55	9.42	19.97	8.15	7.28	15.43	101
3B	15:58-16:58	1.250		6.8		2838	10.15	5.97	16.12	10.36	26.48	12.89	8.29	21.18	100
4A	9/16	1.286	103	6.0	10.4	1493	3.82	3.74	7.56	7.65	15.21	5.88	5.95	11.83	101
4B	17:53-18:53	1.248		6.1		2018	4.12	3.11	7.23	8.33	15.56	5.79	6.68	12.47	98
5A	9/16	1.262	100	6.4	10.1	2310	3.91	4.34	8.25	8.36	16.61	6.54	6.63	13.17	102
5B	19:47-20:47	1.205		6.6		2365	4.40	4.85	9.25	5.20	14.45	7.68	4.32	11.99	99
6A	9/16	1.310	98	5.9	10.4	1516	4.44	3.53	7.97	2.96	10.93	6.09	2.26	8.35	102
6B	21:37-22:37	1.271		6.0		2242	3.74	2.77	6.51	6.60	13.11	5.12	5.19	10.31	99
7A	9/16	1.130	93	6.2	8.8	1641	2.53	1.70	4.23	5.52	9.75	3.74	4.88	8.63	103
7B	23:20-01:20	1.088		6.3		1644	5.62	2.06	7.68	5.32	13.00	7.06	4.89	11.95	100

[a]Includes volume of SO_2, which represented less than 0.3 percent of the sampling volume.

[b]Includes Parr bomb results, which constituted approximately 5 to 20 percent of the total arsenic on the filter.

amount of arsenic found in the front half ranged from 43 to 73 percent of the total. The filter and probe rinse fractions each constituted a considerable portion of the arsenic in the front half, where the filter contributed between 44 and 60 percent of the front-half arsenic.

Table 4-2 presents statistical data for the paired runs. The mean arsenic concentration and standard deviation (mg/dNm^3) for each pair of runs are also presented. The relative standard deviation (RSD) is the standard deviation expressed as a percentage of the paired mean. Front-half data are presented separately from back half data for informational purposes only. Since the Proposed Method 108 requires determination of stack emissions from the total amount of arsenic measured by the train, only the total amount should be considered for statistical purposes. Appendix A outlines the statistical design and calculations for the field tests.

A comparison of the statistical results for the total arsenic in each train indicates that the within-run relative standard deviation for the seven sample runs ranged between 3.9 and 22.8 percent, with the value for the precision of the method at 15.7 percent. Standard deviations of paired runs had a low value of 0.36 mg/dNm^3, a high of 4.06 mg/dNm^3, and a pooled mean of 1.90 mg/dNm^3. The high and low standard deviations do not correspond directly to the high and low RSD values because of the difference in specific arsenic concentrations. The mean arsenic concentration of paired runs ranged from 3.08 to 18.3 mg/dNm^3 based on total arsenic, and the overall mean value was 10.5 mg/dNm^3. Individual run values of total arsenic ranged between 2.82 and 21.2 mg/dNm^3. Considering the sampling site constraints and process variability, these results showed that an acceptable degree of precision was achieved using Method 108.

The range of mean arsenic values is attributed to the use of different sampling points and to variations in the process operation. Three sampling points in two different ports were used in the test series. To decrease sampling run time yet still collect approximately the same sample volume, a different port and point with a higher velocity head were selected after the initial set of paired runs were conducted. Runs 2 through 7 were conducted in the same port. Runs 2 through 6 were conducted at a point approximately 101 cm into the duct, and Run 7 was conducted in the same port but at a point approximately 71 cm into the duct.

TABLE 4-2. STATISTICAL DATA FOR GROUPED ARSENIC RUNS AT PLANT NO. 1

	Front-half arsenic		Back-half arsenic		Total arsenic			
	Concentration, mg/dNm^3		Concentration, mg/dNm^3		Concentration, mg/dNm^3			
Run No.	Run value	Paired mean	Run value	Paired mean	Run value	Paired mean	σ mg/dNm^3[a]	RSD, percent
1A	4.75	5.31	3.60	2.72	8.34	8.02	0.45	5.6
1B	5.86		1.84		7.70			
2A	1.64	1.44	1.69	1.64	3.33	3.08	0.36	11.7
2B	1.24		1.59		2.82			
3A	8.15	10.53	7.28	7.78	15.43	18.30	4.06	22.2
3B	12.89		8.29		21.18			
4A	5.88	5.84	5.95	6.32	11.83	12.15	0.47	3.9
4B	5.79		6.68		12.47			
5A	6.54	7.11	6.63	5.48	13.17	12.58	0.83	6.6
5B	7.68		4.32		11.99			
6A	6.09	5.60	2.26	3.72	8.35	9.33	1.39	14.9
6B	5.12		5.19		10.31			
7A	3.74	5.40	4.88	4.88	8.63	10.29	2.35	22.8
7B	7.06		4.89		11.95			
Overall mean		5.89[b]		4.65[b]		10.53[b]	1.90[c]	15.7[d]

RSD = Relative standard deviation, the standard deviation expressed as a percentage of the mean concentration.

[a]Standard deviation with N-1 weighting for sample data.

[b]Simple averages of tabulated data, $\bar{X}$.

[c]Pooled standard deviation, i.e., $(\Sigma\sigma^2/n)^{\frac{1}{2}}$.

[d]Precision, expressed as coefficient of variation corrected for bias after Zeigler, Technometrics®, May 1973.

The production rate varied during the test series. The furnace charge rate was determined by the number of charges (loads) per hour to the furnace. A charge rate of six loads per hour was established as the baseline condition for determining the furnace production status. Charge rates of greater than six loads per hour were considered representative of maximum production. During testing, the furnace charge rate varied from approximately four loads per hour for the second test conducted to at least six loads per hour or more for Tests 1 and 3 through 7.

Several factors that could have affected test results, including variation in sample rates, test location, and a broken probe liner, are addressed as follows.

The change of sampling point and port locations, coupled with variations in stack gas velocity due to process changes, resulted in a range of sampling rates. The first set of runs was conducted at a sampling rate of approximately 0.012 dNm^3/min, the second at 0.039 dNm^3/min, and the remainder at approximately 0.02 dNm^3/min. Based on the RSD values for total arsenic, the difference in sampling rate of a factor of 2 or 3 did not appear to affect method precision at this emission source.

The sampling site location selected for this test series did not meet minimum Method 1 requirements;[6] however, a better site was not available. The initial velocity traverse of the duct cross section indicated that the spatial variation in velocity head was relatively low near selected sampling point locations. Therefore, gas velocities measured at the two nozzles (5 cm apart) of the dual sampling train configuration were essentially equal, which would eliminate one source of potential bias. Sampling with probes in a vertical downward position could have resulted in a low bias to measured arsenic concentrations; however, because the equipment was handled carefully and acceptable relative standard deviation values were obtained, any such bias is believed to be minimal. A rigid, heated glass connector between the probe and filter holder was used to avoid potential sample losses in the vertical sampling.

At the completion of Runs AEOD-5A and 5B, the sampling trains were capped off and transported to the cleanup area. After the acceptable posttest leak check, the glass probe liner for Run 5B was broken approximately 1 in. from the front end during removal of the nozzle in the sample recovery

area. Because extraneous matter in the sample was limited to pieces of broken glass and because less than 2% of the liner was shattered, the arsenic content of the sample should not be significantly biased. Therefore, Run 5B was accepted as valid.

4.2 PLANT NO. 2

4.2.1 Process Description

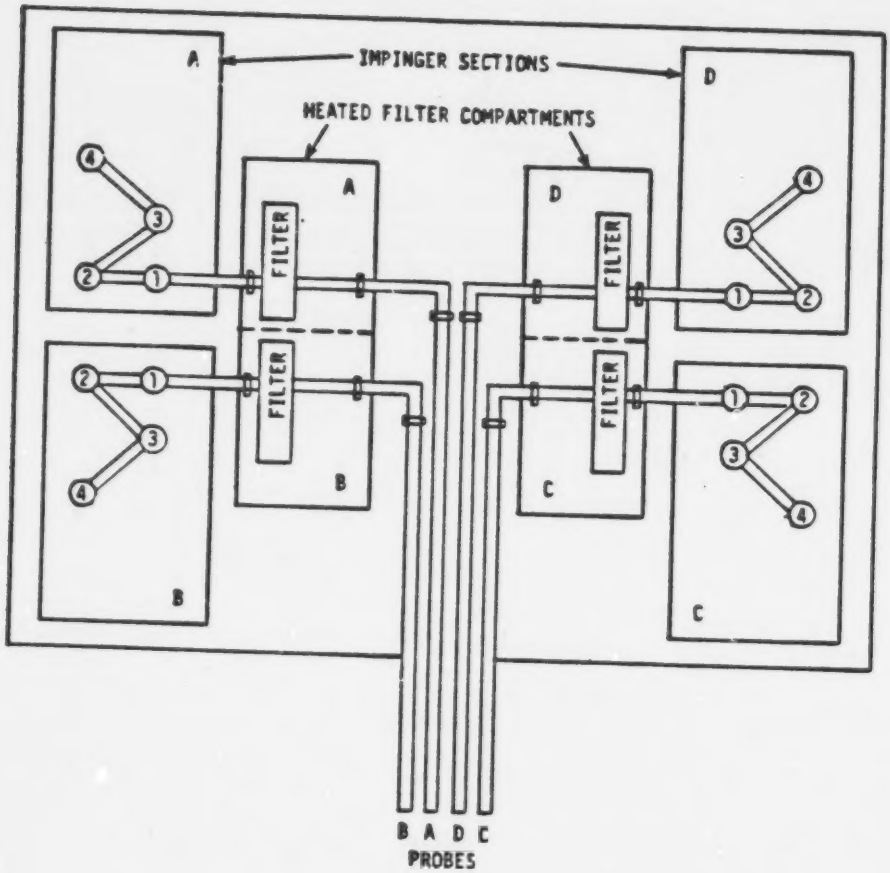
Tests were performed on the uncontrolled emissions from a regenerative natural-gas-fired glass-melting furnace. The furnace evaluated is representative of a moderate capacity glass furnace which produces crystal soda-lime glass using arsenic as a conditioning and refining agent. Furnace pressure is maintained by use of an induced-draft ejector system. The detailed description of the process and process data are presented in a separate report.[5]

4.2.2 Sampling Location and Test Methods

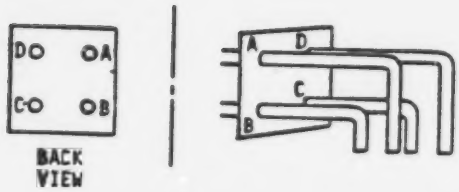
A four-train (quad) sampling system was used to collect samples at the exit stack of the glass-melting furnace. This system allows four trains to sample simultaneously at essentially a single point in the stack.

Because this sampling approach allows four trains to sample simultaneously at essentially a single point, it reduces the effect of variations in the velocity and particulate profiles on the sampling results. It also permits a statistically significant number of samples to be taken in a short amount of time. Further, since all four trains are identical for every run, the within-run precision can be determined at the same time as the relationship of the different trains is being compared. This methodology for determining method precision was developed and validated in a previous EPA study.[8] Nine quad-train runs representing 36 individual samples were collected.

All samples were collected at the furnace exit stack as depicted in Figures 4-4 and 4-5. Ambient ejector air is controlled automatically to maintain furnace pressure and is introduced annularly (see Figure 4-6) at a volume ratio of about 1:1 to the furnace gases. According to plant personnel, the furnace gas temperature is about 760° C (1400° F). Single-point, isokinetic sampling techniques were used in each quad run. Prior to sampling,



QUAD TRAIN ASSEMBLY



PROBE AND NOZZLE ORIENTATION

Figure 4-4. Quad-train configuration.

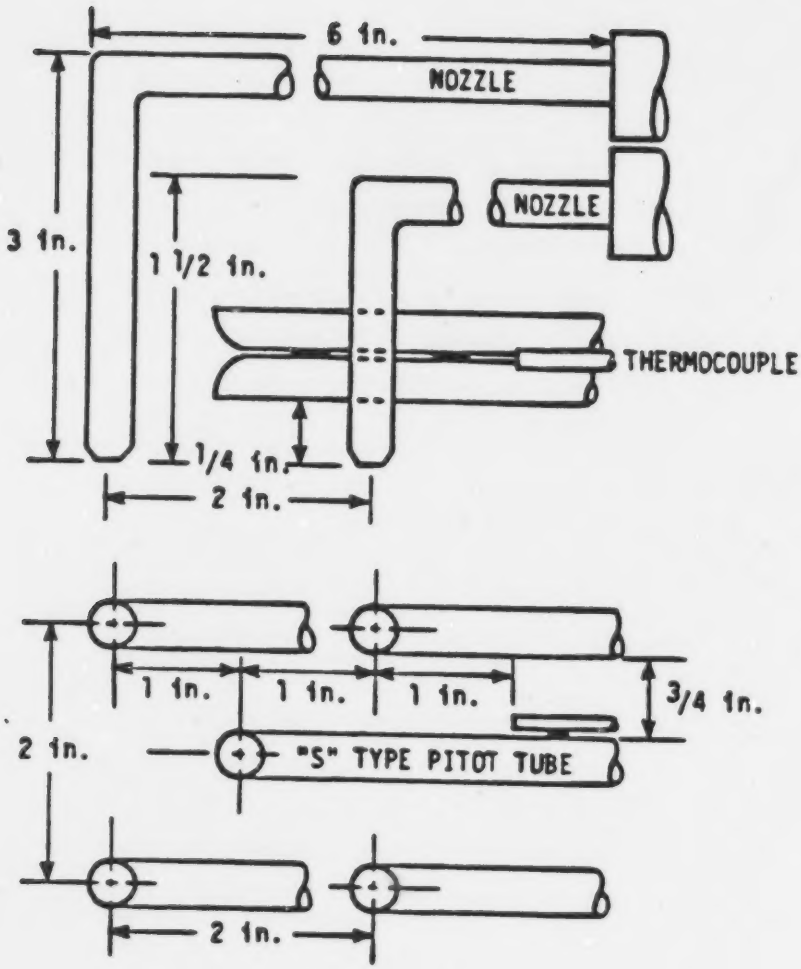


Figure 4-5. Four-train sampling system showing nozzle, pitot tube, and thermocouple position.

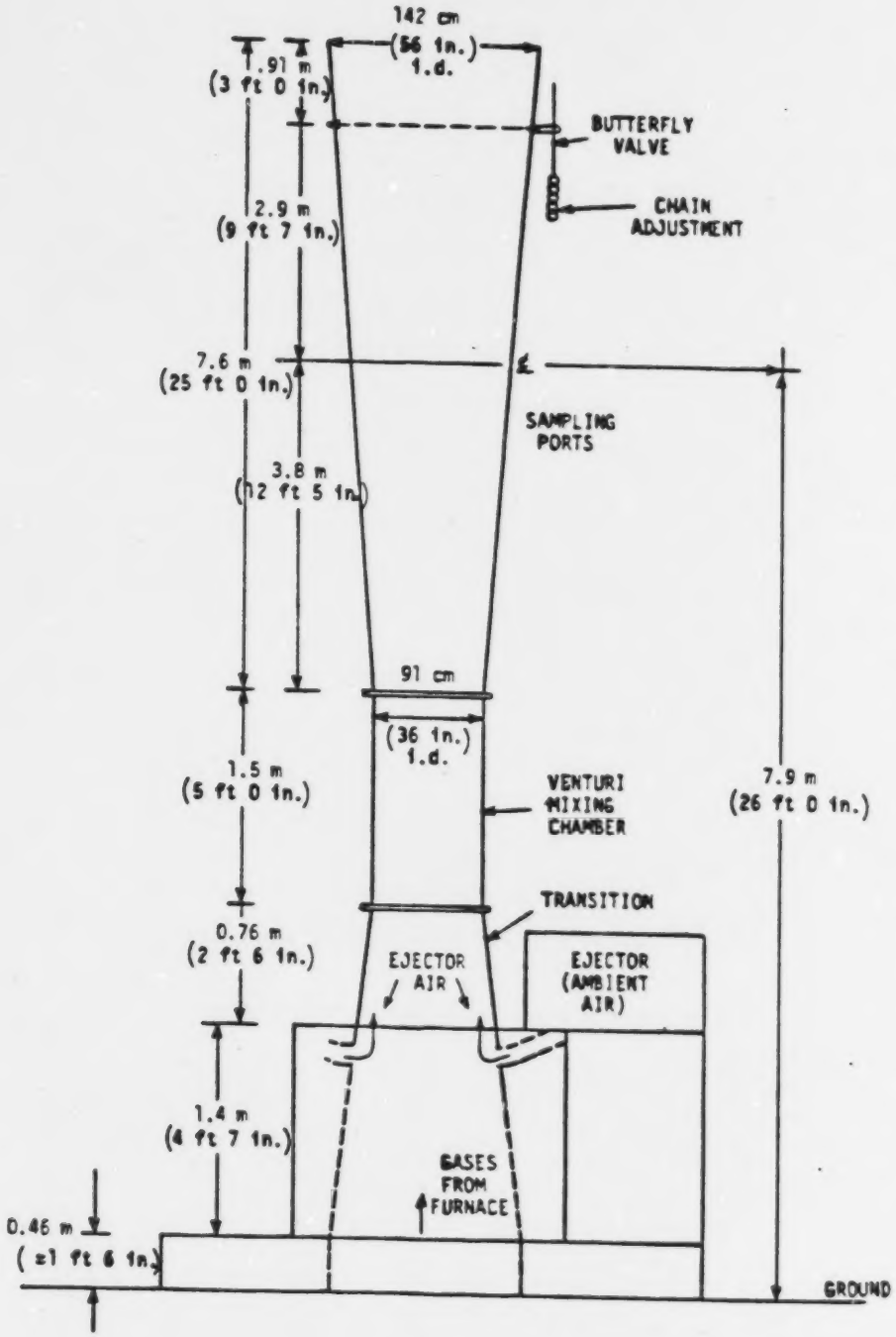


Figure 4-6. Furnace exit stack elevation (no scale).

a complete velocity and temperature profile was established using procedures described in EPA Methods 1 and 2.[6] The temperature velocity traverses indicated a range of ~560° F to 620° F during one test and ~540° to 600° F during another. This demonstrated good mixing of the ambient and furnace gases. Since the emitted particles were estimated at 90% < 1.0 μm, the indicated good mixing of gases, also, indicates a potential of evenly distributed particulate mass. OAQPS ran a traversing Method 108 of this site resulting in a three-run concentration of 8.84 mg/dNm^3 compared to our overall average of 9.59 mg/dNm^3, thereby supporting the conclusion that the arsenic emissions are evenly distributed in the sampling plane. The velocity and temperature data were used to select sample nozzle sizes so as to maintain isokinetic sample rates and ensure adequate sample volume (0.85 dNm^3 [30 dscf]) for each train. The quad nozzle assembly was positioned approximately 52 cm (20.5 in.) from the inside wall of the stack for each run. Sampling rates generally ranged between 0.014 dNm^3/min (0.50 dscf/min) and 0.017 dNm^3/ min (0.60 dscf/min), and sampling times were typically 60 and 70 min.

4.2.3 Sampling and Analytical Procedures

The sampling and analytical procedures used in this test program followed those described in Section 4.1.3 except that the impingers containing hydrogen peroxide (H_2O_2) for SO_2 determination were eliminated due to low (<30 ppm) concentration of SO_2. Based upon this and other data OAQPS has eliminated the H_2O_2 from the method. All tests were conducted isokinetically by regulating the sample flow rate relative to the gas velocity in the stack as measured by the pitot tube and thermocouple attached to the quad sampling probe arrangement.

4.2.4 Test Results

A total of 36 tests (nine quad-train runs) were conducted on an uncontrolled emissions stream from a glass-melting furnace. EPA Proposed Method 108[4] was used to measure arsenic concentrations with one modification. The impingers containing hydrogen peroxide (H_2O_2) were deleted. A Method 108 sample collected prior to testing showed an SO_2 concentration of less than 30 ppm. Since making a correction for this low level of SO_2 would have no significant impact on the sample volume and there was no danger to sampling

equipment or personnel, the train configuration was so modified by deletion of the H_2O_2 impingers as instructed by EPA project personnel. The pretest sample data also verified the expected arsenic concentration (13.5 mg/dNm^3), which aided in the selection of sampling times and volumes for the final test design and in the analytical preparation. Table 4-3 summarizes the sampling results of pretest Method 108.

A four-train (quad) sampling system was used to collect all samples. This system allows four trains to sample simultaneously at essentially a single point in the stack. Consequently, use of such a system reduces the spatial and temporal variations of velocity and pollutant profiles on the sample results. It also permits a statistically significant number of samples to be taken in a short amount of time. As mentioned earlier, Appendix A outlines the statistical design and calculations for the field tests.

Since all four trains are identical for every run, the within-run precision can be determined at the same time that the between-run relationship of the trains is being compared. In each train, the probe and filter temperatures were set at the predetermined temperature (121° C) and monitored throughout each run by use of multiterminal digital indicators; thermocouples were located in each probe and immediately behind the Method 108 filter frits.

Table 4-4 presents the quad-train sampling conditions, Table 4-5 summarizes the arsenic analytical results for each run, and Table 4-6 presents statistical data for the grouped runs.

Sample volumes were consistent and ranged between 0.902 and 1.21 dNm^3. Isokinetic sampling rates ranged from 95.7 to 104.2 percent, which is within the acceptable range of 90 to 110 percent. The probe and filter temperatures represent average values determined from data recorded on the field data sheets. Filter temperatures ranged from 119° to 148° C, and probe temperatures ranged from 118° to 151° C. Note that for the odd-number runs in Train C, the recorded probe temperatures were greater than 200° C. This was attributed to a short in the probe thermocouple wiring (the probe inadvertently remained in the rotation of sample components throughout the test program). The actual probe temperature was at least 100° C for each affected test because the probe was warm to touch and no visible moisture

TABLE 4-3. PRETEST METHOD 108 SAMPLE RESULTS

Run No.[b]	Date (1984) and time (24 h)	Sample volume, dNm^3	Percent moisture,	Gas temperature, °C	Arsenic results[a]		SO_2 content, ppm
					Total train weight, mg	Concentration, mg/dNm^3	
PA-1	5/8 14:26-15:26	1.16	8.0	324	15.81	13.5	<30

[a]Greater than 99 percent of the total arsenic was collected in the front half of the sample train (i.e., nozzle, probe, and filter).

[b]Single-point, isokinetic sample collection techniques were employed.

TABLE 4-4. SUMMARY OF QUAD TRAIN SAMPLING CONDITIONS

Run No.	Sampling type	Date (1984) and time (24 h)	Sampling conditions					
			Metered volume, dNm^3	Percent isokinetic	Percent moisture	Gas temperature, °C	Probe temperature, °C	Filter temperature, °C
1A	Method 108	5/14 10:45-11:55	1.06	102.8	9.1	299	123	126
1B			1.20	98.8	8.7	299	132	124
1C			1.21	101.7	6.9	299	207	121
1D			1.08	104.1	9.3	299	123	120
2A	Method 108	5/14 14:00-15:10	0.956	104.2	9.2	307	123	148
2B			1.00	100.5	9.3	307	135	125
2C			1.03	102.7	9.2	307	193	121
2D			0.965	103.1	9.3	307	151	118
3A	Method 108	5/15 08:35-09:45	0.959	102.9	8.2	307	131	122
3B			1.02	97.7	8.9	307	123	127
3C			1.08	103.0	8.9	307	229	119
3D			0.957	102.6	8.9	307	126	119
4A	Method 108	5/15 12:31-13:31	1.02	101.0	8.3	286	118	143
4B			1.10	99.9	8.0	286	124	138
4C			1.12	100.8	7.9	286	121	120
4D			1.05	101.3	8.6	286	128	121
5A	Method 108	5/15 15:00-16:10	0.913	101.0	8.7	296	132	125
5B			0.973	95.7	8.7	296	132	122
5C			1.04	101.2	8.5	296	226	120
5D			0.902	99.2	8.8	296	123	120
6A	Method 108	5/15 17:21-18:31	0.975	101.0	9.0	312	119	130
6B			1.04	98.9	8.9	312	126	121
6C			1.07	100.9	8.8	312	126	122
6D			0.981	99.6	9.1	312	130	121

(continued)

TABLE 4-4 (continued)

Run No.	Sampling type	Date (1984) and time (24 h)	Sampling conditions					
			Metered volume, dNm^3	Percent isokinetic	Percent moisture	Gas temperature, °C	Probe temperature, °C	Filter temperature, °C
7A	Method 108	5/16 08:58-10:08	0.942	103.8	8.6	302	131	122
7B			1.03	100.8	8.6	302	136	120
7C			1.06	102.6	8.6	302	225	119
7D			0.929	102.0	8.9	302	126	119
8A	Method 108	5/16 11:15-12:15	0.981	101.4	8.2	281	121	125
8B			1.05	100.1	8.0	281	134	123
8C			1.09	102.6	8.0	281	125	128
8D			1.00	101.3	8.3	281	130	123
9A	Method 108	5/16 13:18-14:28	0.976	102.4	8.4	301	130	124
9B			1.07	99.6	8.3	301	132	127
9C			1.09	101.1	8.3	301	252	125
9D			0.969	101.2	8.7	301	124	122

TABLE 4-5. SUMMARY OF QUAD TRAIN RESULTS FOR PLANT NO. 2 (GLASS PLANT)

Run No.	Sample volume, dNm^3	Sample weights, mg					Concentration, mg/dNm^3		
		Probe rinse	Filter[a]	Total front half	Back half[b]	Total train	Front half	Back half	Total train
1A	1.06	1.06	8.57	9.63	<0.05	9.63	9.08	--	9.11
1B	1.20	1.10	9.43	10.53	<0.05	10.53	8.78	--	8.78
1C	1.21	1.00	6.68	7.68	<0.05	7.68	6.35	--	6.35
1D	1.08	1.10	9.11	10.31	<0.05	10.31	9.55	--	6.35
2A	0.956	0.73	7.70	8.43	<0.05	8.43	8.82	--	8.82
2B	1.00	1.17	8.88	10.05	<0.05	10.05	10.05	--	10.05
2C	1.03	1.23	8.27	9.50	<0.05	9.50	9.22	--	9.22
2D	0.965	1.10	7.86	8.96	<0.05	8.96	9.28	--	9.28
3A	0.959	1.14	7.65	8.79	0.087	8.88	9.17	0.09	9.26
3B	1.02	1.31	9.12	10.43	<0.05	10.43	10.23	--	10.24
3C	1.08	1.38	9.57	10.95	<0.05	10.95	10.14	--	10.13
3D	0.957	1.26	8.34	9.60	<0.05	9.60	10.03	--	10.04
4A	1.02	1.00	8.75	9.75	<0.05	9.75	9.56	--	9.53
4B	1.10	1.07	9.15	10.22	<0.05	10.22	9.29	--	9.28
4C	1.12	1.05	8.72	9.77	<0.05	9.77	8.72	--	8.73
4D	1.05	1.30	8.23	9.53	<0.05	9.58	9.08	--	9.17
5A	0.913	1.17	8.52	9.69	<0.05	9.69	10.61	--	10.62
5B	0.973	1.18	9.07	10.25	<0.05	10.25	10.53	--	10.53
5C	1.04	1.32	9.71	11.03	<0.05	11.03	10.61	--	10.62
5D	0.902	1.14	8.26	9.40	<0.05	9.40	10.42	--	10.42
6A	0.975	0.95	8.73	9.68	<0.05	9.68	9.93	--	9.93
6B	1.04	1.18	9.16	10.34	<0.05	10.34	9.94	--	9.96
6C	1.07	1.28	9.29	10.57	<0.05	10.57	9.88	--	9.92
6D	0.981	1.19	9.09	10.28	<0.05	10.28	10.48	--	10.48
7A	0.942	1.16	7.85	9.01	<0.05	9.01	9.56	--	9.57
7B	1.03	1.36	8.03	9.39	<0.05	9.39	9.12	--	9.13
7C	1.06	1.34	9.16	10.50	<0.05	10.50	9.91	--	9.95
7D	0.929	1.22	7.90	9.12	<0.05	9.12	9.82	--	9.82
8A	0.981	1.06	8.98	10.04	<0.05	10.04	10.23	--	10.24
8B	1.05	1.13	9.35	10.48	<0.05	10.48	9.98	--	9.95
8C	1.09	1.17	9.09	10.26	<0.05	10.06	9.41	--	9.44
8D	1.00	1.33	8.24	9.57	<0.05	9.57	9.57	--	9.57

(continued)

TABLE 4-5 (continued)

Run No.	Sample volume, dNm^3	Sample weights, mg					Concentration, mg/dNm^3		
		Probe rinse	Filter[a]	Total front half	Back half[b]	Total train	Front half	Back half	Total train
9A	0.976	1.17	7.62	8.79	0.061	8.84	9.00	0.06	9.06
9B	1.07	1.16	8.70	9.86	<0.05	9.86	9.21	--	9.21
9C	1.09	1.18	8.92	10.10	<0.05	10.10	9.27	--	9.24
9D	0.969	1.21	8.24	9.45	<0.05	9.45	9.75	--	9.76

[a]Reported filter weight includes the Parr bomb arsenic results, which constituted approximately 0.5 percent of the total arsenic on the filter.

[b]Blank values for back-half arsenic analytical results ranged from 0.0 to 0.5 mg, therefore values less than 0.05 mg are not reported.

TABLE 4-6. STATISTICAL DATA FOR GROUPED RUNS FOR PLANT NO. 2

Quad run No.	Concentration, mg/dNm³		σ, mg/dNm³[b]	RSD, percent[c]
	Individual run value	Group mean $\bar{X}$[a]		
1A	9.11			
1B	8.87			
1C	6.35[d]	9.19	0.361	3.90
1D	9.58			
2A	8.82			
2B	10.05			
2C	9.22	9.34	0.514	5.50
2D	9.28			
3A	9.26			
3B	10.24			
3C	10.13	9.92	0.446	4.50
3D	10.04			
4A	9.53			
4B	9.28			
4C	8.73	9.18	0.334	3.60
4D	9.17			
5A	10.62			
5B	10.53			
5C	10.62	10.55	0.100	0.95
5D	10.42			
6A	9.93			
6B	9.96			
6C	9.92	10.07	0.272	2.70
6D	10.48			
7A	9.57			
7B	9.13			
7C	9.95	9.62	0.361	3.80
7D	9.82			
8A	10.24			
8B	9.95			
8C	9.44	9.80	0.365	3.70
8D	9.57			

(continued)

TABLE 4-6 (continued)

Quad run No.	Concentration, mg/dNm³			
	Individual run value	Group mean $\bar{X}$[a]	σ, mg/dNm³[b]	RSD, percent[c]
9A	9.06			
9B	9.21			
9C	9.24	9.32	0.305	3.30
9D	9.76			
Overall means	--	9.67[e]	0.367[f]	3.85[g]

[a] Mean concentration.

[b] Within-run standard deviation with N-1 weighting for sample data.

[c] Within-run relative standard deviation is the standard deviation expressed as a percent of the mean concentration.

[d] This value is an outlier according to the Dixon ratio test.

[e] Simple averages of tabulated data.

[f] Pooled standard deviation $=(\Sigma\sigma^2/n)^{\frac{1}{2}}$.

[g] Precision, expressed as coefficient of variation corrected for bias after Zeigler, Technometrics®, May 1973.

condensation was evident in the glassware connecting the probe to the filter holder. Since the Train C probe rinse within-runs and between-runs data are comparable, the effect on sample results is believed to be insignificant. The moisture content of the stack gas at the sampling point was consistent throughout the test series, and the average gas temperatures ranged from 281° to 312° C.

As presented in Table 4-5, arsenic sample weights are reported in milligrams for each sample fraction. As stated before, the Proposed Method 108 requires the determination of stack emissions from the total amount of arsenic measured by the train. The filter weight includes both the NaOH extract and the Parr bomb (HF/HNO_3 extract) results. These extract results consistently averaged 0.1 mg (approximately 1.0 percent or less of the total arsenic in the filter sample).

Arsenic was found mainly in the front half (probe and filter) of each of the 36 individual trains. The total amount of arsenic found in the front half was at least 99 percent in each case, and approximately 85 percent of this amount was found in the filter fraction. No significant amount of arsenic was present in the back half (impingers). The elimination of back half data <0.05 mg due to the 0.05-mg limit reported in Table 4-5 was established after careful analysis of the sample "blank" data. In summary, 60 percent of the blank values for the NaOH rinse and H_2O impinger solutions were at or below the analytical detection limit (0.002 to 0.005 mg); the remaining blank values ranged up to a maximum value of 0.05 mg. Values below 0.05 mg were considered insignificant because this back-half arsenic content would have constituted less than 0.5 percent of the total arsenic collected, the liquid fraction blank data varied greatly, and 7.7 mg was the minimum amount of arsenic collected in any one train.

The statistical data presented in Table 4-6 show that an acceptable degree of precision was achieved by Method 108. The close within-run agreement between individual trains also indicates that biases from spatial and temporal variations in emissions were minimized effectively. For each group, the mean arsenic concentration and standard deviation are presented in mg/dNm^3. The RSD is expressed as a percentage of the mean.

The standard deviations of the quad runs had a low value of 0.10 mg/dNm^3, a high value of 0.51 mg/dNm^3, and a "pooled" mean value of 0.37 mg/dNm^3. The RSD values ranged from 0.95 to 5.5 percent with the value for the precision of the method at 3.85 percent. The mean arsenic concentration of the individual quad runs ranged from 9.18 to 10.55 mg/dNm^3 with an overall mean of 9.67 mg/dNm^3, which indicated a generally consistent process operation throughout the test period. Individual quad-run values were comparable and ranged from 8.73 to 10.62 mg/dNm^3.

Several factors observed during the test series that could have affected sampling results are addressed as follows.

During the initial quad run, the sampling pump for Train B became inoperable for approximately 3 minutes but was immediately restarted upon correction of the problem. This sampling train was run 3 minutes more than Trains A, C, and D to adjust the sample volume. No further problems of this type were encountered during the remaining quad tests. Preliminary volume and moisture calculations were comparable for each train. Therefore, Train B was considered an acceptable sample and analyzed accordingly.

Also during this initial run, Train D exhibited a posttest leak rate in excess of 0.006 m^3/min (0.2 ft^3/min). The leak was audibly noticeable in the filter holder while the leak check was in progress. This problem was attributable to an improper filter holder glassware piece that, upon cooling, prevented a proper seal of the filter holder assembly. A similar problem occurred in Train A during Quad Run 3. For both runs, a visual inspection of recovered samples showed no difference between any of the within-run samples. Preliminary within-run calculations with no leakage volume adjustments were comparable, particularly the moisture contents, which indicated that the leak did occur during train cool-down or at the very end of the test. Considering this, both runs were accepted as valid samples with no leak correction. As presented in Table 4-5, no significant difference was found between the total arsenic concentrations determined for Samples 1D and 3A when compared with the respective within-run data. Additionally, both runs exhibited similar arsenic distribution characteristics, in that at least 99 percent of the arsenic was found in the front half of the train. Sample 3A was one of two trains that exhibited a back-

half arsenic content exceeding the 0.05-mg reporting limit, which indicated that some leakage around the filter may have occurred. The reported value of 0.087 mg (no blank correction applied) represents approximately 1 percent of the front-half arsenic results for this run. Based on the sampling and analytical results of these runs, the data are considered valid with no leakage corrections applied.

Problems were prevented from occurring on the remaining tests by removing the incompatible glassware components from the equipment rotation and by performing two pretest leak checks: the first on the quad system prior to heating it to test condition temperatures and the second on the quad system after it was heated to test condition temperatures. Pretest leak checks of Runs 1 through 3 were performed on only the not preheated quad system. With the exception of Samples 1D and 3A, no posttest leak problems were encountered.

Several samples recovered from Quad Runs 1 through 3 had an incomplete annulus or ring around the outside edge of the filter. If the filter is aligned properly when placed on the frit and does not shift position when the filter holder is assembled and tightened, there should be a continuous ring around the edge of the filter where no sample is present. An incomplete annulus would indicate possible sample slippage around the filter. Samples 1B, 2D, and 3A, 3B, and 3C exhibited an incomplete annulus. No sample material was observed on any of the frits associated with these runs, however, indicating no slippage around the filter. The back-half results of these runs, with the exception of 3A, support this conclusion since essentially no arsenic was found in the impinger section of these trains.

In Quad Run 3, 0.1 N NaOH was inadvertently placed in the impinger section of each train instead of distilled water as specified in Method 108.

As instructed by the EPA project officer, samples collected during this run were recovered and analyzed using Method 108. This procedural error had no significant impact on sample results as reported in the review of the first document of the literature review section of this report. The back-half arsenic results were comparable to the levels observed in the other quad groups.

Finally, during sample recovery of the third quad run, the front filter holder glassware piece (Train C) was broken prior to rinsing with 0.1 N NaOH. As instructed by the EPA project officer, the pieces of glassware were collected and placed in a sealed container for shipment to the laboratory. The glassware was soaked in 0.1 N NaOH and then analyzed for arsenic according to Method 108. As expected, no arsenic was found in the glass rinse; therefore, any bias to sample results is believed to be minimal.

5.0 QUALITY CONTROL AND QUALITY ASSURANCE PROCEDURES

5.1 QUALITY ASSURANCE

Because the desired end product of testing is to achieve representative emission results, quality assurance is one of the main facets of stack sampling. Quality assurance guidelines provide the detailed procedures and actions necessary for defining and producing acceptable data. Four such documents were used in this test program to ensure the collection of acceptable data and to provide a definition of unacceptable data: the Quality Assurance Project Plan prepared by PEDCo and reviewed and approved by the EPA's EMSL; the EPA Quality Assurance Handbook Volume III, EPA-600/4-77-027; the PEDCo Environmental Emission Test Quality Assurance Plan; and the PEDCo Environmental Laboratory Quality Assurance Plan. The last two, which are PEDCo's general guideline manuals, define the company's standard operating procedures and are followed by the emission testing and laboratory groups.

For this specific test program, the following steps were taken to ensure that the testing and analytical procedures produced quality data:

- Calibration of all field sampling equipment.
- Checks on train configuration and calculations.
- Onsite quality assurance checks (i.e., leak checks of the sampling train, pitot tube, and Orsat line) and QA checks of all test equipment prior to use.
- Use of designated analytical equipment and sampling reagents.
- Internal and external audits to ensure accuracy in sampling and analysis.

The same general QA procedures were followed during both field evaluations. The following subsections describe these activities in detail for each source tested.

5.1.1 Plant Number 1

Table 5-1 lists the sampling equipment used to perform the arsenic tests and the calibration guidelines and limits. In addition to the pre- and posttest calibrations, a field audit was performed on the metering systems and thermocouple digital indicators used for the dual-train arsenic sample runs. Critical orifices constructed by PEDCo were used in the dry gas meter audits. All the calibrations performed in the field in general were found to be within the allowable limits.

As an additional check of the reliability of the method used to analyze the samples, a blank train was assembled in the recovery area, capped off, and set aside for about 2 h. It was then recovered in the same manner as the test samples. The blank train samples were shipped to the laboratory and analyzed by the same procedures as those used for the actual emission samples. In addition to the blank sampling train, aliquots of the reagents used in the collection and recovery of the samples were obtained and analyzed by the same procedures as those used for the actual samples. Table 5-2 presents the results of the blank sample train and reagent analysis. The results are considered reasonable and indicate that background arsenic contamination was not a problem in the sample recovery area. The results of the blanks are relatively small and vary considerably. For this reason the data are reported with no blank corrections applied.

The samples collected each day were shipped by overnight carrier to PEDCo's laboratory in Cincinnati. Samples were received nearly every day between September 16 and October 2, 1983. Sample preparation was initiated the same day the samples were received. Atomic absorption analyses using both flame and furnace techniques were conducted almost daily. Every sample was first analyzed by the flame technique. Samples whose concentrations were below 30 mg/L (30 ppm) were also analyzed using the graphite furnace. The 30-mg/L limit was based on previous experience with Method 108, which indicated good agreement above this level. The flame absorbance of a 30-mg/L standard is approximately 0.08 absorbance unit. As the analyses were completed and the data reduced by the laboratory, the results were reviewed by the QA officer. The QA officer reviewed instrument calibration, the analysis of the standard reference solution (SRS), agreement between

TABLE 5-1. FIELD EQUIPMENT CALIBRATION

Equipment	I.D. No.	Calibrated against	Allowable deviation	Actual deviation	Within allowable limits	Comments
Meter box	FB-1 Train B	Wet test meter	Y ±0.02 Y	+0.004	X	
			ΔH @ ±0.15	-0.09	X	
			(Y ±0.15 Y post-test)	+0.012	X	
	FB-10 Train A			+0.003	X	
				-0.09	X	
				+0.007	X	
Pitot tube	029	Standard pitot tube	Cp ±0.01	-	X	Visually inspected onsite
	390			-	X	
Digital indicator	207	Millivolt signals	±0.5%	-0.30%	X	Maximum deviations
	262			-0.38%	X	
Thermocouple	164	ASTM-3F	±1.5%	-0.63%	X	Maximum deviations
	178			-0.47%	X	
Orsat analyzer	141	Standard gas	±0.5%	-0.3%	X	Maximum deviations
Impinger thermometer	288	ASTM-3F	±2° F	0° F	X	
	290			0° F	X	
Electronic balance	M-1	Type S weights	±0.5 g	-0.5 g	X	Maximum deviations
Barometer	299	NBS traceable barometer	±0.10 in. Hg (0.20 in. Hg post-test)	-0.01 in. Hg (-0.11 in. Hg)	X	

(continued)

TABLE 5-1 (continued)

Equipment	I.D. No.	Calibrated against	Allowable deviation	Actual deviation	Within allowable limits	Comments
Dry gas thermometer	FB-1	ASTM-3F	±5° F	-4.0° F	X	Inlet
	FB-1			-5.0° F	X	Outlet
	Train B					
	FB-10			-2.0° F	X	Inlet
	FB-10			-2.0° F		Outlet
	Train A					
Probe nozzle	Setup 1	Caliper	±0.004 in.	0.001 in.	X	
	Setup 2			0.003 in.	X	

TABLE 5-2. ARSENIC BLANK DATA FOR PLANT NO. 1 TESTS

Sample train arsenic blank[a]			
Filter, mg	NaOH probe rinse, mg	Impinger section, mg	Total train blank, mg
0.55	0.04	0.002	0.59

Reagent blank arsenic values					
Date samples received (1983)	Corresponding AEOD run no.	Filter total, mg	NaOH[b] mg/L	H_2O[c] mg/L	HNO_3[d] mg/L
9/16	1,2	0.33	0.044	0.12	0.018
9/20	3-7	0.81	0.250	0.17	
9/20	3-7	--	0.310	0.22	
Average blank values		0.57	0.201	0.17	0.018

[a]Sample train was fully assembled in recovery area and then recovered and analyzed as a sample.

[b]Between 200 and 419 mL of NaOH was used to rinse the probe. Approximately 100 mL of the NaOH was used to rinse the impingers on both days.

[c]On both days 300 mL of water was added to the arsenic impingers.

[d]This solution was used only to clean equipment in the field.

flame and furnace results, and general consistency of the data. He then prepared a list of samples for reanalysis. Flame and furnace results had to agree within ±20 percent or 0.010 flame absorbance unit, whichever was greater. Samples to be reanalyzed were placed into the continuous analysis process at the appropriate point. Although the samples for this project were received in two shipments, portions of these samples were analyzed on multiple days spanning the entire analysis period. Because samples were integrated into the total sample flow, the results of all the quality control activities are reported.

The following is a summary of the QA activities performed during the analytical phase of this project. Twenty-two batches of samples were analyzed by flame atomic absorption. Fifty-six sets of standards (0, 10, 30, 50, 80, 100 ppm) were analyzed with 22 batches of samples. The average correlation coefficient is 0.9985, out of a range of 0.9997 to 0.9944. The average detection limit is 3.3 ppm. A value of twice the range of the 0-ppm standard above the Y-intercept was used to calculate the detection limit. A standard reference solution independently prepared from As_2O_3 with a nominal value of 150 ppm was analyzed (1:2 dilution) with each set of standards. (Standards were prepared from a commercially available 1000-ppm standard solution.) The average value obtained for the 56 analyses of this SRS was 157.1 ppm, with a standard deviation (SD) of 4.75 ppm (3.0 percent RSD). Only 2 of the 56 determinations fell outside the range of the mean ±2 SD (one was above 167 ppm and one was below 148 ppm). No significant historical data are available for this level of arsenic analysis.

These data indicate that the precision and accuracy of the flame atomic absorption analyses are well within acceptable limits. The percent difference of the average measured value of the SRS and its predicted value is 4.7 percent; the RSD of the measured value is 3.0 percent.

The results of the audit samples supplied by EPA and determined by flame atomic absorption (listed in Table 5-3) are consistent with the data just presented. The relatively large difference at 10 ppm is predictable in that it is only three times the average detection limit.

Table 5-4 presents the results of seven samples checked by the method of standard addition. These analyses were performed early on in the project

TABLE 5-3. AUDIT RESULTS

EPA No.	Lab No.	Volume, mL	Arsenic concentration (EPA values), mg As/L	As conc. measured, mg/L	Total As, mg
B-3-I	DC329	500	10	13.6, 12.6	6.82, 6.29
B-4-I	DC330	500	10	10.8, 12.6	5.42, 6.29
G-1-I	DC331	500	100	103, 105	51.3, 52.7
G-3-I	DC332	500	100	107, 106	53.4, 53.1
H-1-I	DC333	500	40	45.4, 46.1	22.7, 23.0
H-2-I	DC334	500	40	45.7, 48.5	22.9, 24.3

TABLE 5-4. ARSENIC STANDARD ADDITION RESULTS

Lab No.	Spike, ppm	Measured, ppm	Linear regression analysis
DC583 impinger	0	17.51	Slope = 0.783
	10	23.84	Y intercept = 16.97
	20	32.89	Corr. = 0.9979
	30	40.58	X intercept = -21.68
DC581 filter bomb	0	267.2	Slope = 0.9390
	50	301.5	Y intercept = 261.3
	100	353.7	Corr. = 0.9977
	200	451.6	X intercept = -278.3
DC588 filter extract	0	76.23	Slope = 0.9145
	20	95.81	Y intercept = 76.36
	40	111.47	Corr. = 0.9994
	80	149.97	X intercept = -83.50
DC588 filter bomb	0	15.24	Slope = 1.018
	10	26.28	Y intercept = 16.38
	20	39.44	Corr. = 0.9944
	40	55.82	X intercept = -16.09
DC590 impinger	0	13.46	Slope = 0.9571
	10	24.49	Y intercept = 13.89
	20	32.33	Corr. = 0.9989
	40	52.26	X intercept = -14.51
DC591 filter extract	0	99.07	Slope = 0.9938
	20	115.39	Y intercept = 99.20
	40	144.76	Corr. = 0.9927
	80	176.73	X intercept = -99.82
DC599 impinger	0	11.33	Slope = 0.9700
	10	24.85	Y intercept = 13.75
	20	35.88	Corr. = 0.9891
	40	50.83	X intercept = -14.17

to ensure that no significant matrix effects were present. The slopes of all the standard addition analyses were between 0.9 and 1.1 except for that of the first sample, probably because of an error in the spiking solution on the first day. An analysis of the results of the unspiked samples shown in Table 5-4 in the column marked "Measured, ppm" and the X-intercepts shown in Table 5-4 in the column marked "Linear regression analysis" showed less than a 10-percent difference except for Samples DC583 and DC599. The results for DC583 were expected, based on the slope; and the results for DC599 were not unreasonable, inasmuch as this value is at the low end of the calibration curve.

Sixteen batches of samples were analyzed by atomic absorption in which graphite furnace techniques were used. All samples below 30 ppm were analyzed by furnace techniques. Samples between 10 and 30 ppm that did not agree with the flame value within approximately 20 percent were reanalyzed by both flame and furnace techniques. Forty-three sets of standards (0, 0.01, 0.05, 0.10, and 0.15 mg/L) were analyzed with the 16 batches of samples. Twelve of the data sets were reduced by linear regression analysis. The remaining four sets were fitted to a second-degree polynomial. The average correlation coefficient for the linear regression analysis is 0.9984, from a range of 0.9996 to 0.9938. The average correlation coefficient for the polynomial fit is 0.9985, from a range of 0.9987 to 0.9983. The average detection limit for the graphite furnace is 0.0031 ppm. A value of twice the range of the 0-ppm standard above the Y-intercept was used to calculate the detection limit.

A standard reference solution independently prepared from As_2O_3 with a nominal value of 0.0750 ppm was analyzed with each set of standards. (Standards were prepared from a commercially available 1,000-ppm standard solution.) The average value obtained for the 43 analyses of this SRS is 0.0759 ppm with a standard deviation of 0.0036 (4.7 percent RSD). All of the 43 determinations were within ±2 SD of the mean. Historically, the mean value for this SRS is 0.0762, with a standard deviation of 0.0027. The values obtained for the SRS solution during this project are in good agreement with our historical data. These data indicate that the precision and accuracy of the furnace atomic absorption analyses are well within acceptable limits. The difference between the average measured value of

the SRS and its predicted value is 1.2 percent; the RSD of the measured value is 4.7 percent.

No standard addition was performed with the furnace method because the large dilutions required made this impractical. Furnace dilutions usually ranged between 1:40 and 1:200.

One final quality check of the data was performed. Sample extracts were split with Plant No. 1. The plant analyzed all samples above 20 ppm by flame atomic absorption and all samples below 20 ppm by a pyridine-SDDC colorimetric method. The data generated by the two laboratories agreed very well. The overall average difference between the data was less than 10 percent.

5.1.2 Plant Number 2

The sampling equipment used to perform the arsenic tests in this field test is similar to that described in Table 5-1. In addition to the pre- and posttest calibrations, field audits were performed on the metering systems and thermocouple digital indicators used for the sample runs. The onsite audits were conducted at the beginning, middle, and end of the test program. The results of the three field audits indicate that the sample equipment was functioning properly throughout this test series and within the calibration guidelines established by EPA.

As an additional check of the reliability of the method used to analyze the samples, two blank trains were assembled in the recovery area, capped off, and set aside for about 2 h. The first blank train was assembled at the beginning of the test series using clean glassware. On the same day as Runs 7, 8, and 9, the second blank train was assembled with glassware used during previous sampling runs. The blank trains were recovered in the same manner as the test samples. These samples were shipped to the laboratory and analyzed by the same procedures as those used for the actual emission samples. In addition to the blank sampling train, aliquots of the field reagents used in the collection and recovery of the samples were obtained daily and analyzed by the same procedures as those used for the actual samples. Table 5-5 presents the results of the blank sample trains and field blank analyses. The results are considered reasonable and indicate that background arsenic contamination was not a problem in the sample

TABLE 5-5. ARSENIC BLANK DATA FOR PLANT NO. 2

Blank sample train arsenic values[a]				
Train No.	Filter, µg	NaOH probe rinse, µg	Impinger section, µg	Total train blank, µg
1	32.8	8.0	22.2	63.0
2	30.8	7.8	11.6	50.2

Field blank arsenic values				
Date samples taken	Corresponding run No.	Filter total, µg	NaOH,[b] mg/L	H_2O,[c] mg/L
5/11	1st blank train	31.7	0.0854, 0.0346	0.0066
5/14	1-3	27.7	<0.0050	<0.0050
5/15	4-6	30.3	0.0054	0.0363, <0.0066
5/16	7-9	31.5	<0.0050	<0.0050
Average blank values		30.3	--	--

[a]Sample train was fully assembled in recovery area and then recovered and analyzed as a sample.

[b]Between 238 and 387 mL of NaOH was used to rinse the probe. Between 263 and 355 mL of the NaOH was used to rinse the impingers. The maximum blank for the NaOH corresponds to 33 µg for the probe rinse and 30 µg for the impinger samples.

[c]On both days 300 mL of water was added to the arsenic impingers. The maximum blanks for the water correspond to 11 µg.

recovery area. The results of the blanks are relatively small and vary considerably.

Laboratory reagent blank analyses were performed before, during, and after the analysis of the field samples. The results of these analyses are presented in Table 5-6. The average value for six filter blanks was 30.8 µg out of a range of 27.7 to 32.8; a blank correction of 31 µg was used to correct all the reported data. Sixty percent of the blank values for the rinse and impinger samples were at or below the analytical detection limit of 2 to 5 µg; the remaining blank values ranged up to a maximum of 50 µg. Because of the variability of the blank, no average value was determined and no blank corrections applied.

Values below 50 µg were considered insignificant and not reported because 7,680 µg (6,680 on the filter) was the minimum amount of arsenic determined in any train and the blanks for the liquid sample fractions varied considerably.

Each sample was first analyzed by the flame technique. Samples whose concentrations were below 30 mg/L were also analyzed using the graphite furnace. Actual sample concentrations were either greater than 100 or less than 10 ppm. The 30-mg/L limit was based on previous experience with Method 108, which indicated good agreement above this level. As the analyses were completed and the data were reduced by the laboratory, the results were reviewed by the QA officer. The QA officer reviewed instrument calibration, the analysis of the SRS, agreement between flame and furnace results, and general consistency of the data.

The majority of the analysis was performed in three batches by flame atomic absorption. Twenty-seven sets of standards (0, 10, 30, 50, 80, 100 ppm) were analyzed with the samples. The average correlation coefficient is 0.9992, out of a range of 0.9996 to 0.9987. The average detection limit is 2.3 ppm. A value of twice the range of the 0-ppm standard above the Y-intercept was used to calculate the detection limit. A standard reference solution independently prepared from As_2O_3 with a nominal value of 150 ppm was analyzed (1:2 dilution) with each set of standards. (Standards were prepared from a commercially available 1,000-ppm standard solution.) The average value obtained in the 27 analyses of this SRS was 156.9 ppm, with a

TABLE 5-6. ARSENIC LABORATORY REAGENT BLANK DATA FOR PLANT NO. 2

Date (1984)	Filter total, µg	Rinse,[a] mg/L	Impinger,[b] mg/L
5/10	9.1	<0.0076	<0.0076
5/25	11.3	0.0701	0.0701
6/1	2.7	<0.0050	<0.0050

[a]Between 238 and 387 mL of sample was received as the rinse fraction. The maximum laboratory reagent blank corresponds to 27 µg for this fraction.

[b]Between 630 and 719 mL of sample was received as the impinger fraction. The maximum laboratory reagent blank corresponds to 50 µg for this fraction.

standard deviation of 4.00 ppm (2.5 percent RSD). Only 1 of the 27 determinations made fell outside the range of the mean ±2 SD (one was 166 ppm). These data compare very well with the data obtained during the analysis of samples from Plant No. 1.

These data indicate that the precision and accuracy of the flame atomic absorption analyses are well within acceptable limits. The percent difference of the average measured value of the SRS and its predicted value is 4.6 percent; the RSD of the measured value is 2.5 percent.

The results of the audit samples supplied by EPA and determined by flame atomic absorption (listed in Table 5-7) are consistent with the data just presented. The relatively large difference at 10 ppm is predictable in that it is only five times the average detection limit. These data are consistent with the results obtained during the analysis for Plant No. 1.

Ten samples were checked by the method of standard addition. The slopes of all the standard addition analyses are between 0.9 and 1.1 except for those of DM697 which is probably due to an error in spiking, and DM688 and DM660 which are probably due to the fact that the zero spike value was determined to be "less than" a given value (<4.9 ppm). Since a "less than" value does not allow the quantification of the actual value, it is unusable for comparison with the X-intercept value. It is worthy of note that the X-intercept value is in both cases less than the above zero spike determination. An analysis of the results of the unspiked samples and the X-intercepts (standard addition values) revealed that only one sample showed a significant difference. The results of standard addition show no consistent bias attributable to the sample matrices.

The samples were analyzed by atomic absorption in which graphite furnace techniques were used. All samples below 30 ppm were analyzed by furnace techniques. Sample concentrations were either greater than 100 ppm or less than 10 ppm. Values obtained from flame and furnace techniques cannot be accurately compared below 10 ppm because this value is too close to the flame detection limit. Twenty-one sets of standards (0, 0.01, 0.05, 0.10, and 0.15 mg/L) were analyzed with the samples. All the data sets were reduced by linear regression analysis. The average correlation coefficient for the linear regression analysis was 0.9970, out of a range of

TABLE 5-7. AUDIT RESULTS FOR PLANT NO. 2

EPA No.	Lab No.	Volume, mL	Arsenic concentration (EPA values), mg As/L	As conc. measured, mg/L	Total As, mg
B-3-I	DC329	500	10	10.2	5.12
B-4-I	DC330	500	10	11.7	5.83
G-1-I	DC331	500	100	111	55.6
G-3-I	DC332	500	100	107	53.3
H-1-I	DC333	500	40	43.9	22.0
H-2-I	DC334	500	40	43.9	22.0
B-3-I[a]	DC329	500	10	11.1	5.54
B-4-I[a]	DC330	500	10	10.7	5.34
WP-475[a] Conc. 6	DM562	1000	0.207-0.393	0.356	0.356

[a]Graphite furnace analysis.

0.9990 to 0.9954. The average detection limit for the graphite furnace was 0.0035 ppm. A value of twice the range of the 0-ppm standard above the Y-intercept was used to calculate the detection limit.

A standard reference solution (SRS) independently prepared from As_2O_3 with a nominal value of 0.0750 ppm was analyzed with each set of standards. (Standards were prepared from a commercially available 1,000-ppm standard solution.) The average value obtained for the 21 analyses of this SRS was 0.0756 ppm with a standard deviation of 0.0029 (3.9 percent RSD). All except 1 of the 21 determinations were within ±2 SD of the mean. The one value outside these limits was 10.0 percent high. Historically, the mean value for this SRS is 0.0762, with a standard deviation of 0.0027. The values obtained for the SRS solution during this project are in good agreement with our historical data. These data indicate that the precision and accuracy of the furnace atomic absorption analyses are well within acceptable limits. The difference in the average measured value of the SRS and its predicted value is 0.8 percent; the RSD of the measured value is 3.9 percent.

The results of audit samples analyzed using the graphite furnace were listed in Table 5-7. These values are consistent with the previous value and the accepted values. The results of duplicate analyses are presented in Table 5-8. The absolute value of the percent difference was calculated according to the following equation:

$$\text{Percent difference} = \frac{X_1 - X_2}{\bar{X}}$$

where X_1 and X_2 are the individual values and $\bar{X}$ is the average of X_1 and X_2.

Filter samples were analyzed using flame atomic absorption, and all other sample fractions were analyzed using the graphite furnace technique.

The first 14 values reported are based on duplicate analyses of the same sample aliquot on the same day using the same calibration curves. Except for three values at or near the detection limit, the agreement is very good. The average percent difference of the remaining 11 pairs is 2.7 percent.

TABLE 5-8. DUPLICATE ANALYSES DATA FOR PLANT NO. 2

Sample fraction	Arsenic, μg	Difference, %
Filter	9290, 9340	0.5
	8140, 8120	0.2
	8870, 9200	3.7
	8210, 8110	1.2
Bomb	107, 109	1.9
	77.8, 81.2	4.3
	171, 169	1.2
Rinse	1190, 1130	5.2
	1180, 1160	1.70
	1240, 1180	5.0
Impinger	12.4, 9.0	31.8[a]
	<4.4, <3	--[a]
	111, 117	5.3
	5.3, 6.3	17.2[a]
Filter[b]	6680, 6520	2.4
	8570, 9220	7.3
	8060, 8070	0.1
	7490, 7410	1.1
	7750, 9010	15.0
	8570, 9060	5.6
	8160, 7960	2.5
Bomb[b]	307, 331	7.5
Rinse[b]	973, 1020	4.7
NaOH field blank	10.8, 26.6	84.5[a]
H_2O field blank	<2.0, 10.9	--[a]
Impinger[c]	73, 14	136[a]
	57, 13	126[a]
	52, 11	130[a]
	114, <8	--[a]
Rinse[c]	1100, 1230	11.2
	1260, 1110	12.7
	1170, 1080	8.0
	1340, 1200	11.0
	1180, 988	17.7

[a]Near detection limit.

[b]Analyzed on different days.

[c]Sample prepared on different days.

The next nine values reported are based on repeat analysis of the same sample aliquot on different days using different calibration curves. The agreement is good, and only one pair of samples showed a percent difference greater than 10 percent. The average percent difference for these nine values is 5.1 percent.

The last 11 values reported are based on repeat analysis of different sample aliquots on different days using different calibration curves. The first six of these values are very close to the detection limit. The percent differences calculated for these samples are typical of precision near the detection limit. The last five of these values were obtained using the graphite furnace. These concentrations are between 2 and 5 ppm and the samples were diluted 1:50 prior to analysis. The samples were prepared and analyzed on two separate days. The average difference is 12.1 percent for these five values.

6.0 REFERENCES

1. Riggin, R. M., Mezey, E. J., and Henry, W. M., "A Literature Review on Occurrence and Methodology for Determination of Nickel, Chromium, Manganese and Arsenic Species In Air; PB 84-17210J (EPA 600/4-84-026) March 1984.

2. National Research Council, Arsenic: Medical and Biological Effects of Environmental Pollutants National Academy of Sciences, Washington, DC 1977.

3. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Marcy 1979.

4. Method 108 Quality Assurance Evaluation for Arsenic-Copper Smelters, PEDCo Environmental Inc. EPA Contract No. 68-02-3767, Task 66, Dec. 1983.

5. Summary Test Report, "Evaluation and Validation of Proposed EPA Method 108," PEDCo Environmental Inc. EPA Contract No. 68-02-3767, Task 66, July 1984.

6. Federal Register, EPA Reference Methods 1, 2, 3, 4, and 5, 40 CFR 60, Appendix A, July 1983.

7. Federal Register, EPA Proposed Method 108, 40 CFR 61, Appendix B, July 1983.

8. Mitchell, W. J., and M. R. Midgett, "A Means to Evaluate the Performance of Stationary Source Test Methods," Env. Sci. Tech. 10:85-88, 1976.

APPENDIX A

FIELD TEST DESIGN AND STATISTICAL ANALYSIS OF DATA

APPENDIX A

FIELD TEST DESIGN AND STATISTICAL ANALYSIS OF DATA

Field Test Design

The precision of a measurement method based upon actual sampling at stationary sources can be determined by performing separate runs of multiple identical coincidental samples. A dual train produces two identical coincidental samples (X_1 and X_2), and a quad train produces four (X_1 through X_4).

Seven separate runs of a dual train setup (14 total field samples) were performed at a copper smelter. Nine separate runs of a quad train setup (36 total field samples) were performed at a glass plant. These samples were adequate for a determination of the precision of the proposed Method 108, and the specific numbers of total samples at each plant were the maximum permitted by the limitations of time, sampling site availability, and test funds.

Field Test Statistical Analysis of Data

The following formulae were used to calculate the field statistical data.

Plant #1

1. Paired mean for the desired run I through VII = $\bar{X}_I = (X_1 + X_2)/n$

where

X_1, X_2 = arsenic concentrations, individual train values;
n = number of trains (sample size) in the dual train (2)

2. Standard deviation, $\sigma = \left[\frac{(X_1 - X_2)^2}{n}\right]^{\frac{1}{2}}$

3. Relative standard deviation (RSD), % for each run I through VII = $[\sigma/\bar{X}_I](100)$

4. Pooled standard deviation $= \left[\frac{\sum_{i=1}^{N} \sigma_i^2}{N}\right]^{\frac{1}{2}}$

where

N = number of runs (sets of dual train samples) (7)

5. Precision, expressed as RSD, coefficient of variation*, % $= \frac{C \sum_{i=1}^{N} (RSD)_i}{N}$

where

C = 1.2533 is a correction factor for bias*

Plant #2

1. Group mean for the desired run I through IX = $\bar{X}_I = (X_1 + X_2 + X_3 + X_4)/n$

where

X_1, X_2, X_3, X_4 = arsenic concentrations, individual train values;

n = number of trains (sample size) in the quad train (4)

2. Standard deviation, $\sigma = \left[\sum_{i=1}^{n} (X_i - \bar{X})^2/(n-1)\right]^{\frac{1}{2}}$

where

$\bar{X}$ = group mean average for the desired run.

3. Relative standard deviation (RSD) % for each run I through IX $= [\sigma/\bar{X}_I]\ (100)$.

4. Pooled standard deviation $= \left[\frac{\sum_{i=1}^{N} \sigma_i^2}{N}\right]^{\frac{1}{2}}$

where

N = number of runs (sets of quad train samples) (9)

5. Precision expressed as RSD, coefficient of variation*, % $= \frac{C \sum_{i=1}^{N} (RSD)_i}{N}$

where

C = 1.0854 is a correction factor for bias*

* After Ziegler, Technometrics®, May 1973